Calcium-Mediated Catalytic Hydroamination and Hydrophosphanylation Reactions

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MARIE CURRIE

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Abbreviations

Abbreviation	Full-name
Al	Aluminum
Au	Gold
AIBN	2,2′-Azobis-(2-methylpropionitrile),2-(azo(1-cyano-1-ethylethyl)) methylpropane nitrile
Ba	Barium
Ca	Calcium
CN	coordination number
Co	Cobalt
Cs	Caesium
Cy	Cyclohexyl
DME	as solvent used 1,2-Dimethoxyethane
Dme	coordinated 1,2- Dimethoxyethane
dppp	Diphenylphosphanopropane
dppe	1,2-Bis-(diphenylphosphano)ethane
Et	Ethyl
Et_2O	Diethylether
Eu	Europium
Fe	Iron
Ga	Gallium
Gd	Gadolinium
Het	Heteroatom
Hg	Mercury
Hf	Hafnium
HMDS	hexamethyldisilazide
i	iso / ipso
In	Indium

i-Pr	Isopropyl
Ir	Iridium
J	coupling constant
L	Ligand
La	Lanthanum
Lu	Lutetium
M	Metal symbol
m	Multiplet
m	meta
Me	Methyl
Mes	2,4,6- Trimethylphenyl
Mg	Magnesium
Nd	Neodymium
Ni	Nickel
NMR	nuclear magnetic resonance
O	oxygen
o	ortho
p	para
Ph	Phenyl
Pd	Palladium
Pt	Platinum
pk_a	the negative base-10 logarithm of the acid dissociation constant of a solution.
pmdta	*N,N,N',N'',N''*-Pentamethyldiethylentriamine
Pr	Praseodymium
R, R`, R``	Alkyl
Ru	Ruthenium
RT	room temperature
s	singlet
Sc	Scandium
Sr	Strontium

Sm	Samarium
t	triplet
Ta	Tantalum
t-Bu	*Tert*-Butyl, 2,2 dimethylpropane-1-yl
Tf	Triflate
Th	Thorium
THF	as solvent tetrahydrofuran
thf	as coordinated solvent tetrahydrofuran
THP	as solvent tetrahydropyran
thp	as coordinated solvent tetrahydropyran
TMEDA	*N,N,N′,N′*-Tetramethyl-ethylendiamine
Ti	Titanium
Y	Yttrium
V	Vanadium
Yb	Ytterbium
Zr	Zirconium
δ	Chemical shift

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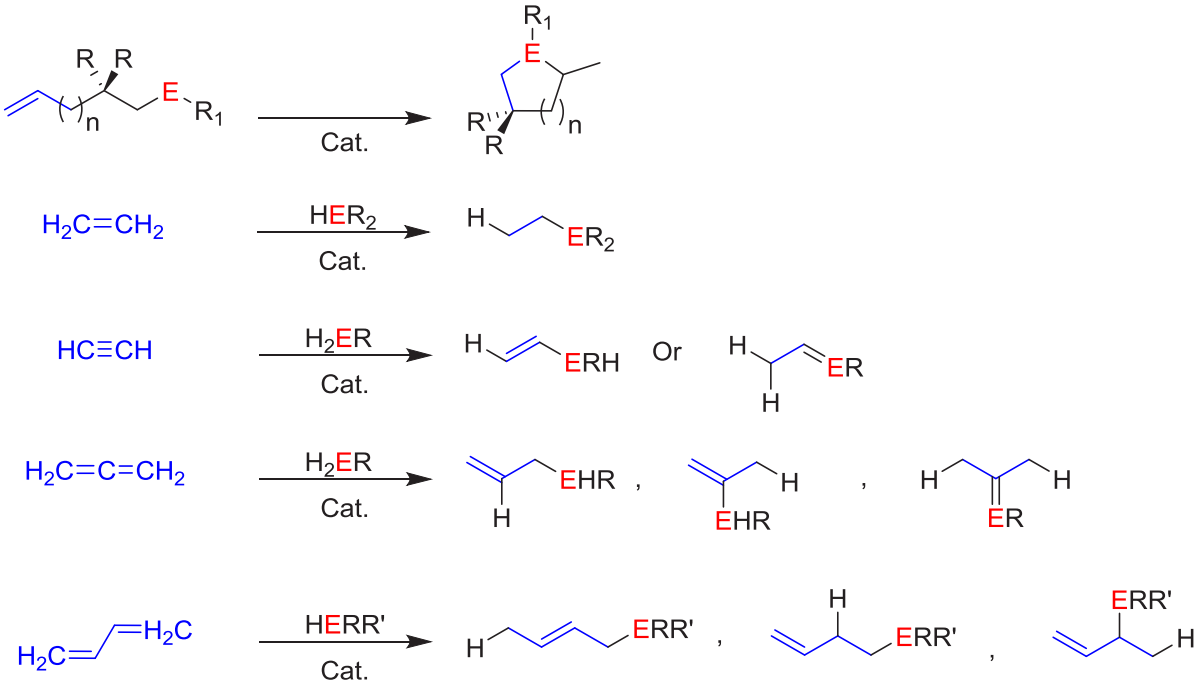
1 Introduction

Platinum had been reported as the first catalyst for industrial production of sulfuric acid in 1746 by *J. ROEBUCK* using the lead chamber process.[1] Since then, catalysts represent the corner stones of the development of new approaches in organic synthesis, medicinal chemistry, preparation of biologically active and pharmaceutical molecules, as well as in numerous applications related to material science and molecular electronics. Recent advances in green and sustainable chemistry emphasized the key role of waste-free chemicals production.[2] Increasing demand in complex molecular structures enforces implementation of sophisticated multistep synthetic procedures and further complicates the waste/product balance. So far most of the commodity chemicals remain to be produced by classical procedures, which are not considered as green.[3] The catalytic production of organic molecules is one of the most important applications of organometallic chemistry.[4] Hydrofunctionalization reactions open the way to form **carbon-heteroatom** bonds with environmentally friendly chemical transformations. Hydrofunctionalization of unsaturated organic molecules via direct addition of H-E (E = Se, S, O, P, N) to multiple bonds is an atom-economical addition reaction which does not produce wastes.[5] In view of the need of green and sustainable chemical procedures, the role of the metal catalysis is crucial to control the reaction, in particular with respect of regio-, stereo-, and enantioselectivity. To accomplish hydrofunctionalization reactions, various metal-based catalysts such as alkali metals (Li),[6] alkaline earth metals (Mg, Ca, Sr, and Ba),[7] group (III) transition metals Y[8] and Sc[9], lanthanoides Ln and actinoides An,[10] group (IV) transition metals Ti[11] and Zr[12], group (V) transition metals (e.g. V & Ta),[13] other transition metals like Fe,[14] Pd,[15] Hg,[16] Ru,[17] as well as post-transition metals like Al,[18] In,[19] and Bi[20] have been investigated.

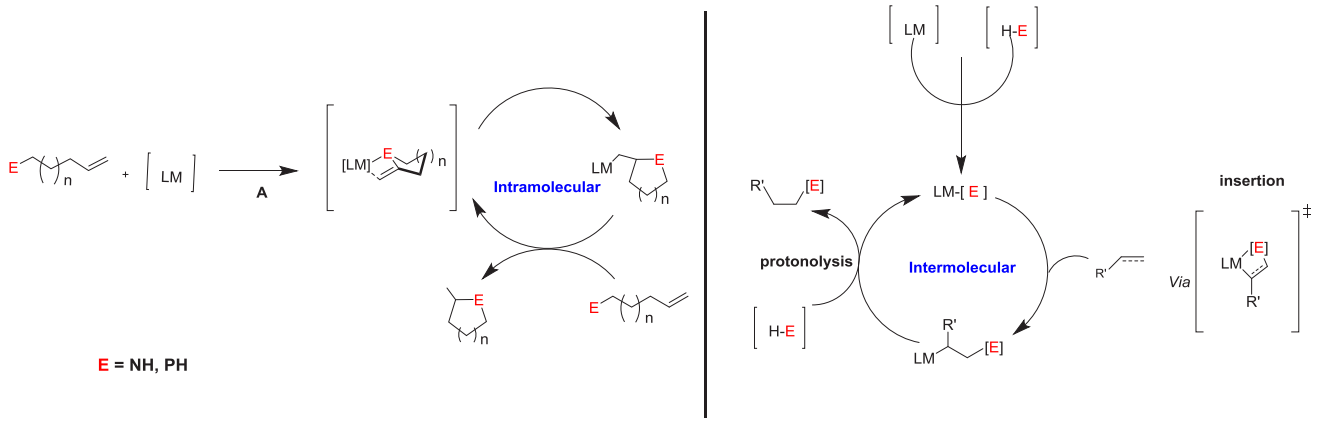
1.1 Hydrofunctionalization - An Overview

Hydrofunctionalization is defined as an addition of a H-E (E = Se, S, O, P, N) bond across a multiple bond, in most cases a carbon-carbon multiple bond of an alkene, alkyne, allene or diene in the presence of proper catalyst (**Scheme 1.1**). Three classes of hydrofunctionalization that are termed as hydrochalcogenation (addition of H-Se, H-S or H-O), hydrophosphanylation (addition of H-P), hydrophosphoranylation (addition of H-P(O)), and hydroamination (addition of H-N) will be discussed.



Scheme 1.1: Catalyzed hydrofunctionalization reactions of alkene, alkyne, allene or diene.

Hydrofunctionalization occurs either via an intramolecular or an intermolecular manner as shown in **Scheme 1.2**.

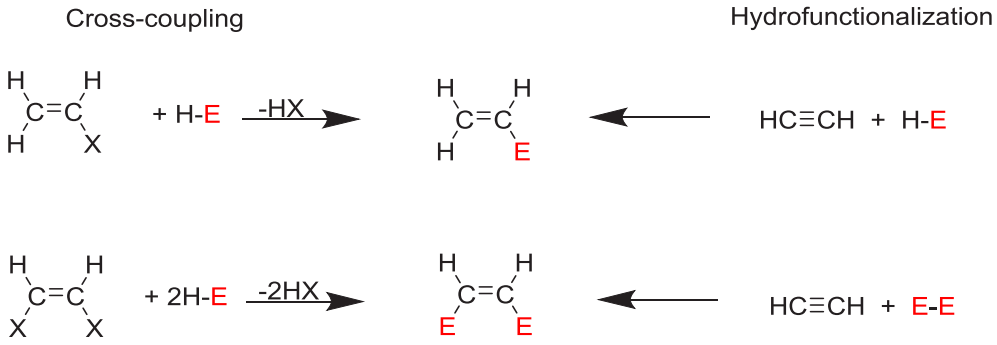


Scheme 1.2: Proposed catalytic cycles for intramolecular and intermolecular hydrofunctionalization reactions.

To achieve the H-E addition, many factors play an important role:

1- Polarity of the H-E bond, electronegativity difference of H and E, determined by the Brönsted acidity of E.
2- The nature of the catalyst: electrocatalyst, organocatalyst, enzymes and biocatalyst, mono- or multinuclear catalyst, as well as naked catalyst or metal-free catalysts;[21] $[Ph_2N^-][Me_4N^+]$ and $[Ph_3C][Me_4N^+]$.
3- Reaction parameters: homo- / heterogeneous conditions, temperature, pressure, and solvent.

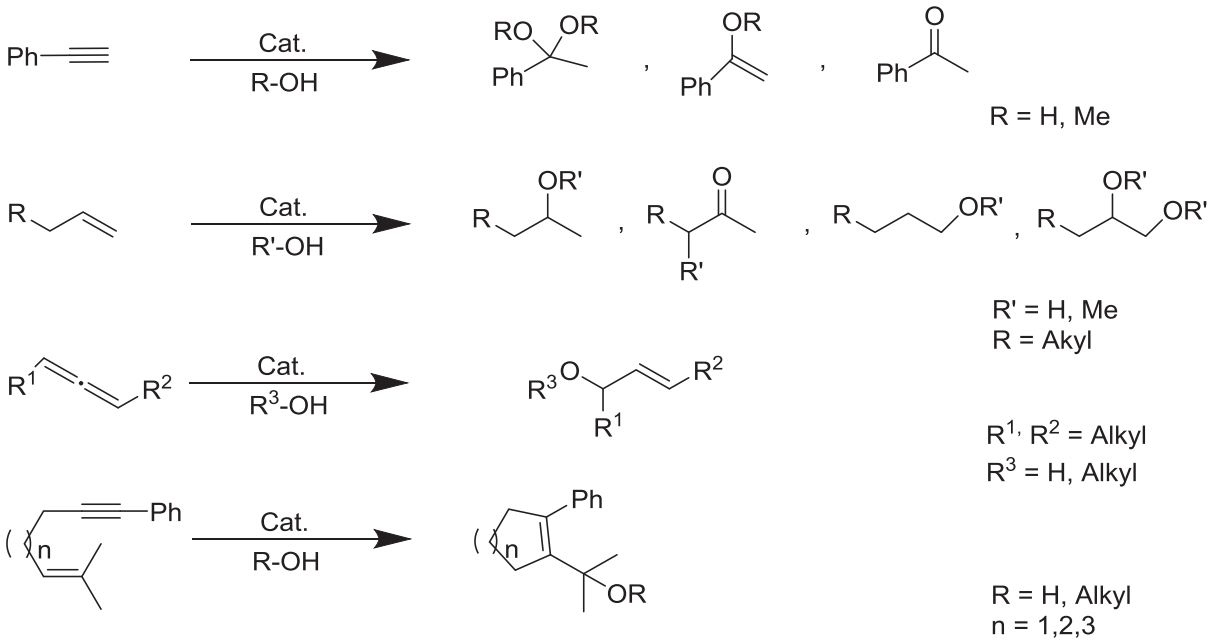
Formation of carbon-heteroatom C(SP^2)-E bonds in vinyl compounds can take place via two powerful approaches; either via cross-coupling[22] or via hydrofunctionalization as shown in **Scheme 1.3**. However, the former usually also yields by-products and requires a multistep synthesis in order to form C-E bonds, whereas hydrofunctionalization is a single step addition process, using often commercially available and inexpensive starting materials.[23]



Scheme 1.3: Formation of C-E bonds either via cross-coupling or via hydrofunctionalization reactions.[3]

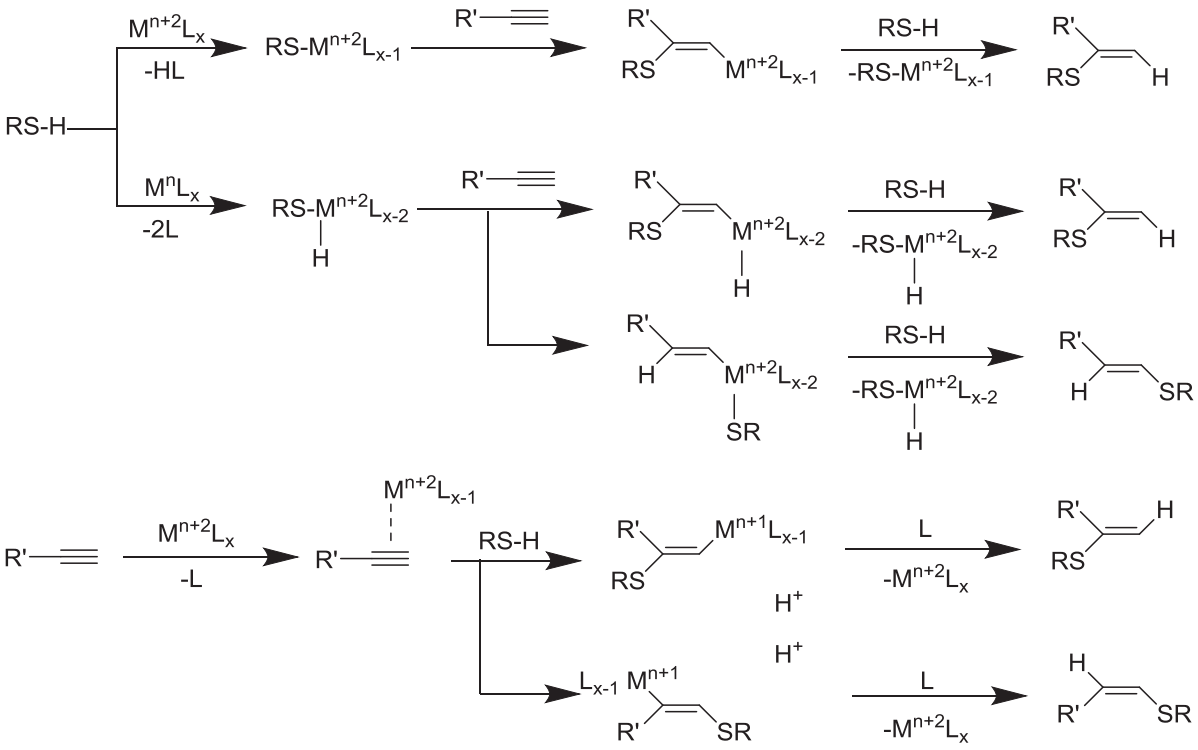
1.2 Hydrochalcogenation (E = O, S, and Se)

The addition of water or alcohols across unsaturated carbon-carbon bonds is one of the main synthetic methods to prepare ketones, ethers, epoxides, lactones, acetales and other oxygen containing compounds. Due to this fact many tireless efforts have aimed at improving the efficiency of the hydration and the hydroalkoxylation of alkynes,[24] alkenes[24a, 24e-g, 25], allenes[24a, 24e-g, 25] as well as hydroxycyclization and alkoxycyclization of enynes[26] using a variety of catalysts such as Au(I),[26c, 27] or Au(III)[28], Brönsted acids, Pt,[28a] Hg,[26c] Rh,[29] Ir, Ni,[30] Pd, and Ga[31] (**Scheme 1.4**).



Scheme 1.4: Examples of hydration and hydroalkoxylation process of alkynes, alkenes, allenes as well as hydroxycyclization and alkoxycyclization of enynes, respectively.

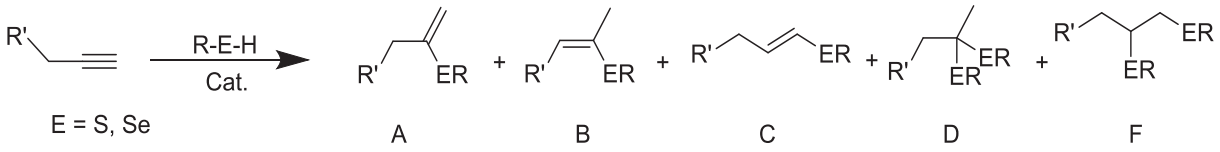
Equally important to the formation of carbon-oxygen bonds is the formation of carbon-sulfur bonds, due to the large number of various sulfur-containing natural and pharmaceutical products,[32] as well as the increasing demand of sulfur-containing ligands and chiral auxiliaries in synthetic chemistry.[33] Hence, thiols have been widely employed as sources of ligands for various transition metals. Generally, the reactions between thiols and transition metal complexes, which are mostly used in order to form the carbon-sulfur bonds, have two path ways: either the ligand-exchange reaction between high-valent transition metal complexes ($M^{n+2}L_x$) and thiols to give the complexes afford only thiolate ligands (RS-$M^{n+2}L_{x-1}$), or the oxidative addition of thiols to low valent transition metals (M^nL_n) to give the corresponding transition metal complexes having both hydride and thiolate ligands as shown in **Scheme 1.5**.



Scheme 1.5: Mechanistic pathways for hydrothiolation of alkynes.

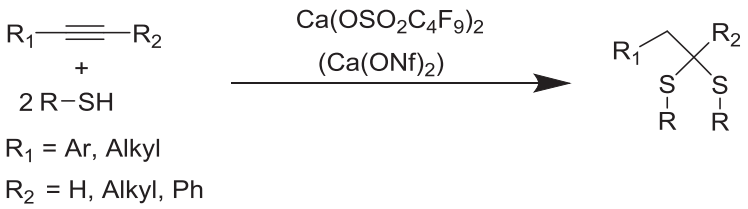
The reaction of the former complexes ($RS\text{-}M^{n+2}L_{x-1}$) with carbon-carbon unsaturated organic compounds such as alkynes may proceed via thiometallation, in which a relatively bulkier $M^{n+2}L_{x-1}$ is bonded at the terminal carbon of alkynes. In the reaction of the latter complexes ($RS\text{-}M^{n+2}L_{x-2\text{-}H}$) with alkynes both of the hydrometallation and thiometallation processes are possible. These processes proceed via syn-addition. An alternative pathway for the addition of thiols to alkynes involves coordination of alkynes to transition metals followed by nucleophilic addition of thiols (or thiolate anions) to the alkynes. These processes take place via anti-addition. By controlling these pathways, regio- and stereoselective hydrothiolation of alkynes is expected to be attained successfully. Hydrothiolation of alkynes was reported in 1949[34] with thioacetic acid and rediscovered in 2009.[35] Various catalysts have been applied to achieve the formation of sulfur-carbon bonds such as Pd, Ni, Pt, Rh,[36] indium(III) bromide,[37] AIBN,[38] Th, U,[39] Au,[40] and caesium carbonate.[41] It is worth here to mention that the hydrothiolation of terminal alkynes (**Scheme 1.6**) leads to many different products: Markovnikov-type adduct (A), Markovnikov addition and then double-bond-isomerization

product (B), anti-Markovnikov adduct (C), double hydrothiolation product (D), and bisthiolation product (F).



Scheme 1.6: Product selectivity in hydrothiolation and hydroselenation of terminal alkynes.[36, 42]

The addition of Se-H bonds to terminal alkynes matches the same results of hydrothiolation (**Scheme 1.6**). Generally, the formation of selenium-carbon bonds shows high similarity to the formation of sulfur-carbon bonds. Moreover, the oxidative addition of selenols to low-valent transition metals, ligand-exchange reactions between high-valent transition metal complexes and selenols and protonation processes of carbon-metal bonds are more efficient than the hydrothiolation. This difference in reactivity is attributed to the greater acidity of selenols ($pK_a = 5.9$ {PhSeH}) compared to PhSH ($pK_a = 6.5$), and the bond energy Se-H (73 kcal/mol) is smaller than that of S-H (87 kcal/mol).[43] The use of transition metal catalysts makes it possible to attain highly regio- and stereoselective syntheses of a variety of vinylic and allylic sulfides and selenides. These reactions are very useful in terms of the synthesis of organosulfur and selenium compounds and also the development of bioactive compounds and new materials. For example, π-conjugated polymers including heteroatoms[44] are promising in material science and these research fields require highly selective methods for introduction of heteroatom groups involving oxygen, sulfur and selenium. Very recently, hydrothiolation reactions catalyzed by Lewis-acidic Ca complexes such as $Ca(OTf_2)_2$, $Ca(NTf_2)_2$, $Ca(NTf_2)_2/Bu_4NPF_6$, $Ca(OSO_2C_4F_9)_2$ and $Ca(ONf)_2$, have been reported and evaluated as efficient catalysts for bis-hydrothiolation of alkynes affording anti-Markovnikov dithioacetals (**Scheme 1.7**).[45]



Scheme 1.7: Calcium-catalyzed hydrothiolation reactions.[45]

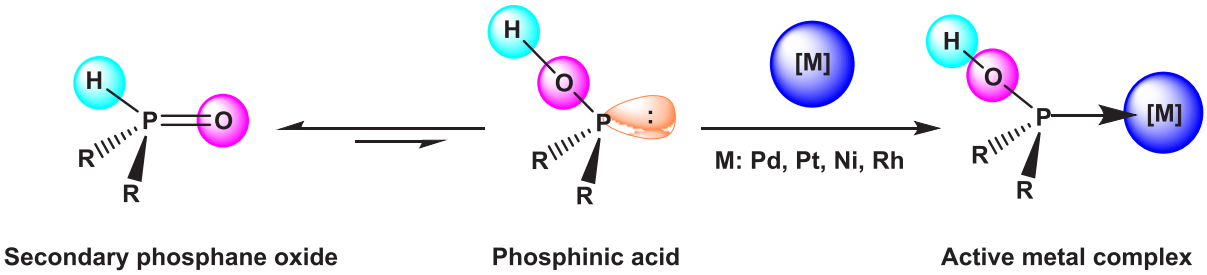
1.3 Hydrophosphanylation & Hydrophosphoranylation

The chemistry of hydrophosphanylation and hydrophosphoranylation has grown explosively over the last decade, as it leads to organophosphane products despite the very small electronegativity difference between P, C, and H according to the diagonal relationship of C and P in the periodic table and similar *ALLRED-ROCHOW* electronegativities (P 2.06, C 2.5, H 2.20). Primary and secondary phosphanes can easily be deprotonated yielding phosphanides R_2P^-. These products can be widely employed in many research areas such as organic and organometallic syntheses. Furthermore, these reactions offer an efficient method to the syntheses of asymmetrically substituted phosphanes and phosphane oxides.[46]

1.3.1 Early and late transition metal catalyzed H-P/ H-P(O) addition

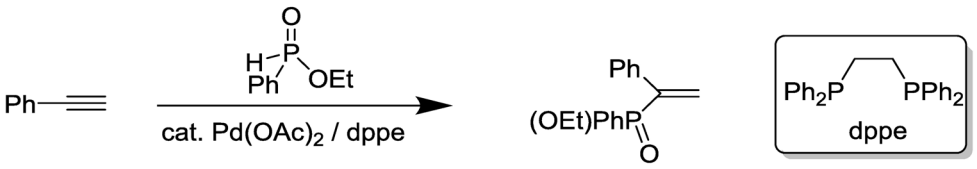
In each hydrofunctionalization reaction early and late transition metals,[47] which are stabilized by Lewis bases such as primary or secondary phosphanes or phosphane oxides, have been used as catalysts. Phosphane and phosphane oxide were attractive coligands for many reasons: (i) weak donors as Lewis and Brönsted bases compared to the hard donors oxygen and nitrogen, (ii) phosphane is a stronger acid (π-acidity is due to P-C σ* anti-bonding orbitals) than ammonia with the formal oxidation state (-III),[48] (iii) the lone pair of the P atom in phosphanes interacts with various soft transition metals leading to an active

metal complex (**Scheme 1.8**) which can be used as catalyst to accomplish the H-P/ H-P(O) addition across an unsaturated c-c bond.[49]



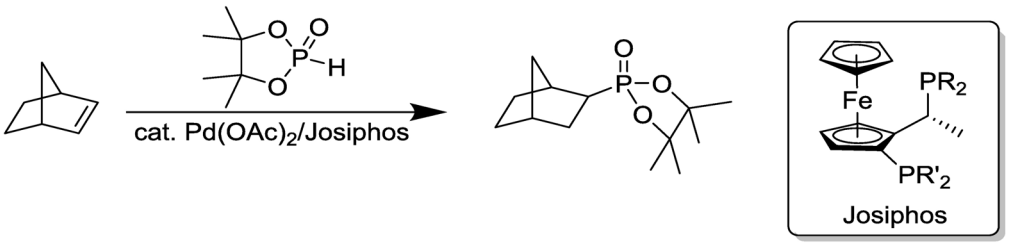
Scheme 1.8: Coordination of Phosphane and phosphane oxides to transition metals.[49]

The transition metal-based catalysts were extensively used to hydrophosphanylate or hydrophosphoranylate alkenes,[50] alkynes,[51] or other unsaturated backbones such as carbodiimides.[52] Due to the availability of d-orbitals which can easily and reversibly change their participation in bonding situation, intermediate reactions like the oxidative addition and the reductive elimination are supported[49b]. Moreover, the catalyst compounds which contain the d^0 metal ions are the mediators for the activation of the strong multiple bonds such as carbon-carbon or carbon-oxygen multiple bonds[53]. For example, hydrophosphoranylation and hydrophosphanylation can be performed successfully with many transition metal-based catalysts[24d, 46b, 54]. Markovnikov or anti-Markovnikov selectivity in hydrophosphanylation of alkynes depend on the metal catalyst and the reaction conditions. The product distributions are thought to be controlled by the regioselectivity of insertion of an alkyne into an M-H or M-P bond. For example, Pd-catalyzed addition of $HP(OR)_2(O)$ to a terminal alkyne was branched selectively, while $HP(O)Ph_2$ preferentially gave linear products. However, a Pd(dppe) catalyst resulted in Markovnikov selectivity both for diphenylphosphane oxide[55] and the mixed substrate HP(Ph)(OEt)(O) (**Scheme 1.9**).



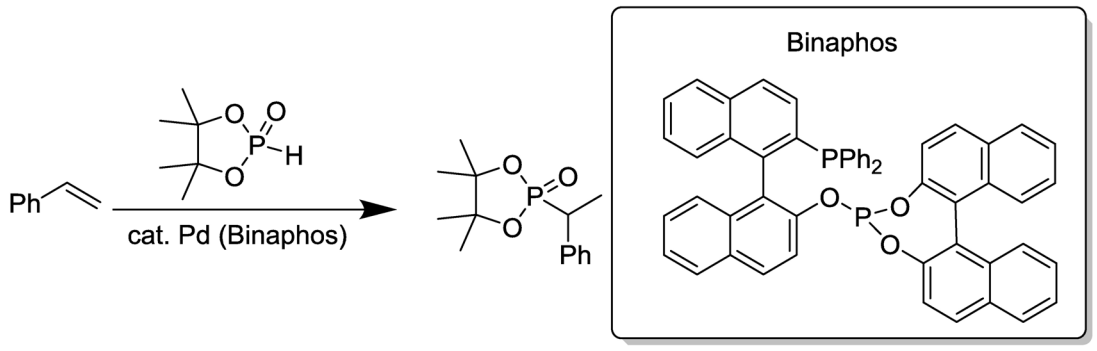
Scheme 1.9:Markovnikov-selective Pd-catalyzed hydrophosphanylation of phenylacetylene.[55]

In 2007 *OGAWA* et al. reported Pd-catalyzed hydrophosphanylation without P-H bonds in the substrate. For instance, the addition of tetraphenyldiphosphane (Ph_2P-PPh_2) to alkynes gave vinylphosphanes, where the alkyne was the source of the "missing" H.[56] Several Pd-catalyzed asymmetric syntheses with mediation of many ligands such as (S, S)-BCPM, (R)-BINAP, (S,S)-BPPM, (S,S)-CHIRAPHOS, (S,S)-DIOP, (R)-MOP, (S)-NMDPP, (R,R)-NORPHOS, (R)-QUINAP, (R)-Tol-BINAP, Trost-ligand, and Josiphos have been also reported for the hydrophosphoranylation of alkenes. For example the Pd-(Josiphos) catalyst enabled the enantioselective hydrophosphoranylation of Norbornene (**Scheme 1.10**).[57]



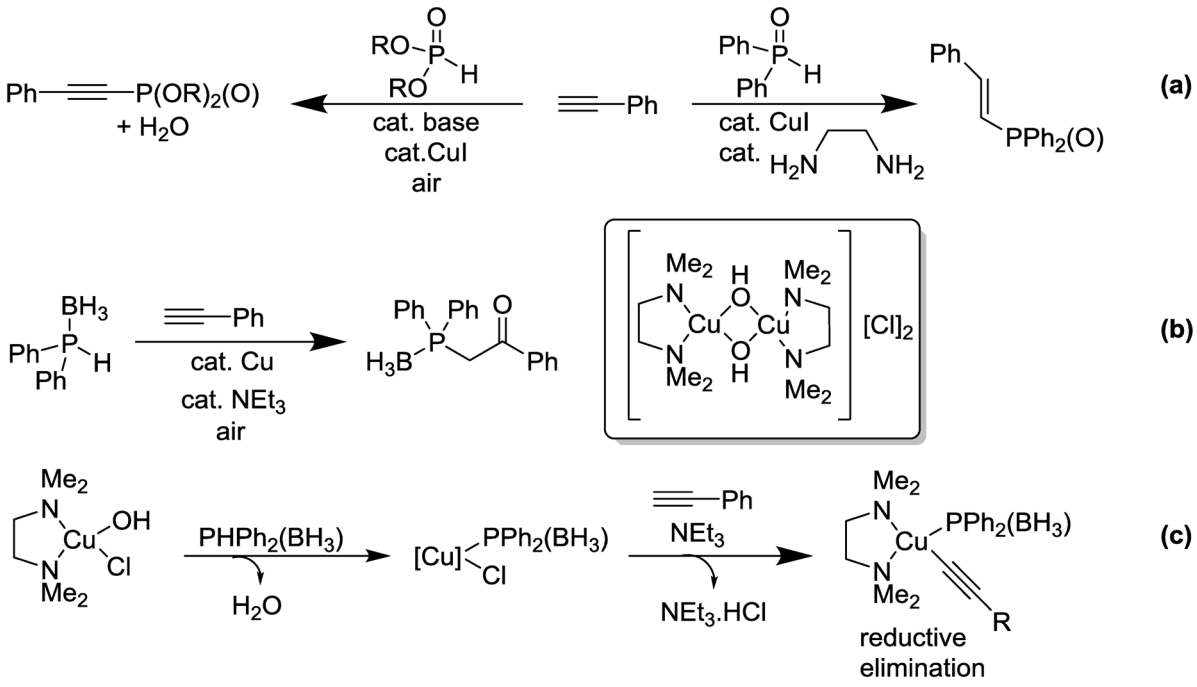
Scheme 1.10: Pd(Josiphos)-catalyzed asymmetric hydrophosphoranylation of norbornene.[57]

Hydrophosphoranylation reactions of styrenes catalyzed by Pd/Binaphos have also been reported. (**Scheme 1.11**).[58] Up to 74% ee for the favored branched isomer was observed with a Pd(Binaphos) catalyst (**Scheme 1.11**).[58]



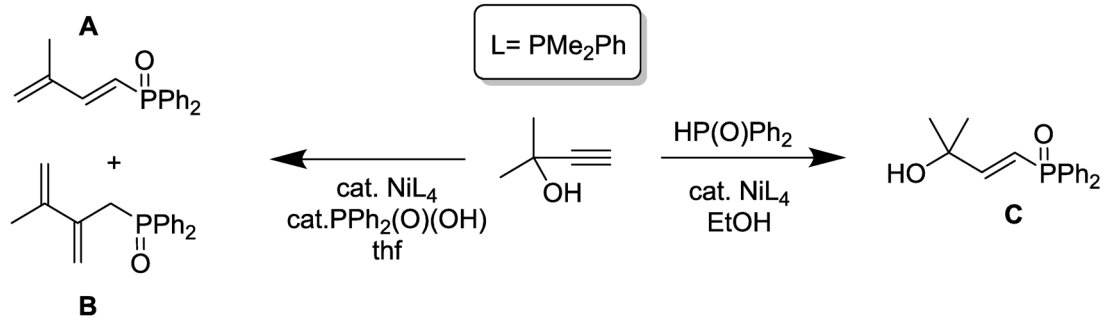
Scheme 1.11: Pd(Binaphos)-catalyzed asymmetric hydrophosphoranylation of styrene.[58a]

Expensive and noble metals like Pd are not always required and thereafter important copper-based catalysts were also extensively used. For example a CuI/ethylenediamine catalyst promoted regioselective addition of diphenylphosphaneoxide to terminal alkynes to yield *E*-alkenylphosphane oxides (**Scheme 1.12a**).[59] Copper based catalysts were also used extensively (in similarity to Pd catalysts) not only for the addition of the P-H, but also for the formation of C-P bonds via cross-coupling of alkynes with phosphaneboranes, which was followed by surprising oxidation of the carbon atom yielding ketones (**Scheme 1.12b**).[60] The formation of the ketone was proposed to occur via a mechanism involving an active species, a copper phosphanido–borane complex, that is formed by a proton transfer to a Cu-OH group according to **Scheme 1.12c**. Formation of a Cu-acetylide followed by P–C reductive elimination would then produce a phosphano-alkyne, whose subsequent Cu-mediated aireal oxidation affords the ketone. The final step in **Scheme 1.12c** is similar to that suggested for nickel or palladium catalyzed cross-coupling of terminal alkynes with chlorophosphanes to give phosphanoalkynes.[61]



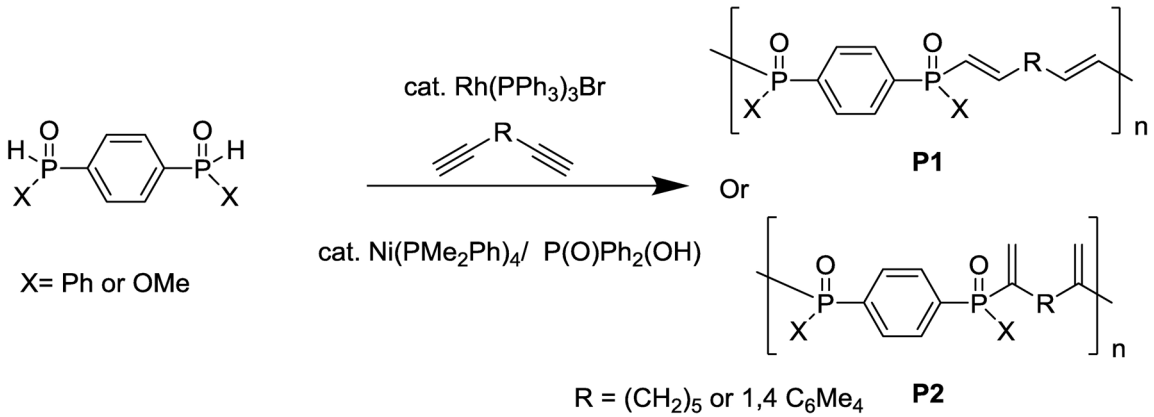
Scheme1.12: Cu-catalyzed hydrophosphanylation, hydrophosphoranylation and cross-coupling of a phosphane-borane and phenylacetylene.[59-61]

Transition metals catalyzed hydrophosphanylation and hydrophosphoranylation processes have also been performed using a Ni-based catalyst. In **Scheme 1.13**
Scheme 1.13, hydrophosphanylation of propargyl alcohols is catalyzed by $Ni(PMe_2Ph)_4$ in the absence and presence of a modifier, O=PPh2(OH). The anti-Markovnikov product **C** was obtained when the catalysis was performed in EtOH solution without $O=PPh_2(OH)$. On the other hand, the presence of the modifier led to the production of the butadiene derivatives **A** and **B** that are formally derived by dehydration of **C**.[62]



Scheme 1.13: Nickel-catalyzed hydrophosphoranylation of a propargyl alcohol. [62]

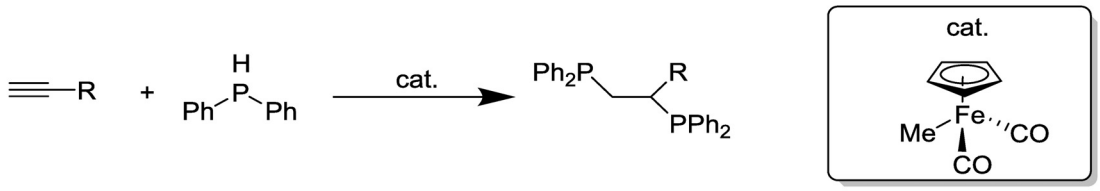
In fact, controlling the regio-, stereo- or chemoselectivity can be of great importance in hydrofunctionalization reactions. According to **Scheme 1.14**, two polymerization products are formed (P1 or P2) depending on the catalyst used. The polymer P1 was obtained when the catalyst $Rh(PPh_3)_3Br$ was used whereas the polymerization led to P2 in the case of catalysis with $Ni(PMe_2Ph)_4/O{=}PPh_2(OH)$).[63]



Scheme 1.14: Control of regiochemistry by metal catalyst in hydrophosphoranylation polymerization of diynes.[63-64]

Double hydrophosphanylation is especially challenging as the product would be a bidentate phosphane that may act as a ligand and coordinate to the metallic center of the catalyst more strongly, according to the chelate effect, than a monodentate phosphane (in the usual hydrophosphanylation) would have coordinated. Recently, *NAKAZAWA* and coworkers reported the iron half sandwich complex $CpFe(Me)(CO)_2$ as the first catalyst toward a regioselective double hydrophosphanylation of alkynes.[65] Double- or Di-

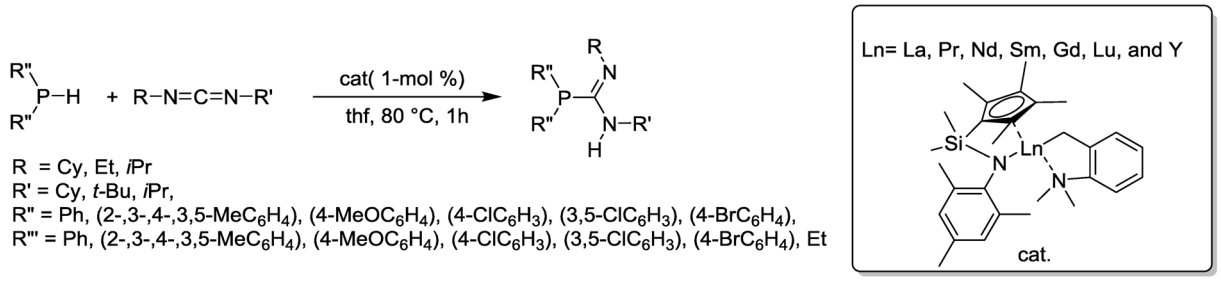
hydrophosphanylation of a series of terminal alkynes was successfully accomplished using the catalyst $CpFe(Me)(CO)_2$ that afforded bisphosphanes in excellent regioselectivity (**Scheme 1.15**).



Scheme 1.15: Iron catalyzed double hydrophosphanylation.[65]

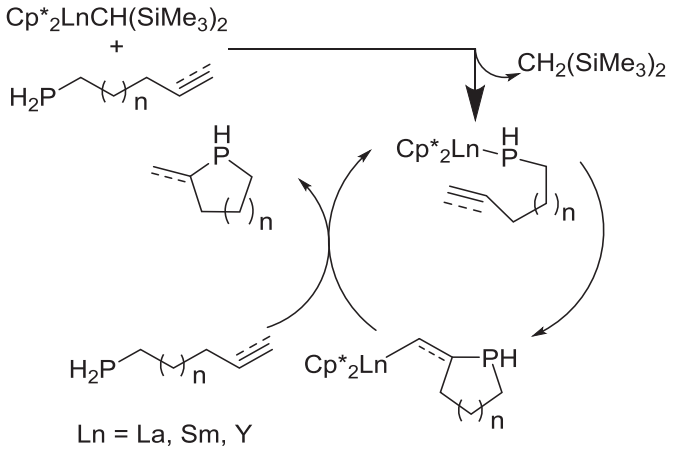
1.3.2 Lanthanoide-catalyzed H-P/H-P(O) addition

Lanthanoides rival the early and late transition metals for catalyzing the hydrophosphoranylation and hydrophosphinylation processes due to the fact that lanthanoides possess many properties like size of the atom/ ion, flexibility and the possibility to behave as Lewis-acids as well as Lewis-bases in the reaction.[66] Furthermore, organolanthanoide complexes are electronically less saturated and sterically more accessible than the ordinary metallocenes of transition metal analogues that have two cyclopentadienyl ancillary ligands.[67] Thus, plenty of properties made the customized catalyst system a rapidly developing area.[68] *HOU* and coworkers synthesized and characterized a series of half-sandwich *o*-dimethylaminobenzyl complexes of Lanthanoides (Sc, Y, La, Pr, Sm, Nd, Gd, Lu) bearing silylene-linked cyclopentadienyl-amido ligands. [69] These complexes serve as efficient catalyst precursors for the catalytic addition of various phosphane P-H bonds to carbodiimides and have led to the formation of a series of phosphaguanidine derivatives in very good yields (**Scheme 1.16**). *HOU* and coworkers pointed out that the increase in the size of the rare-earth metal leads to a significant enhancement of the catalytic activity.[69]



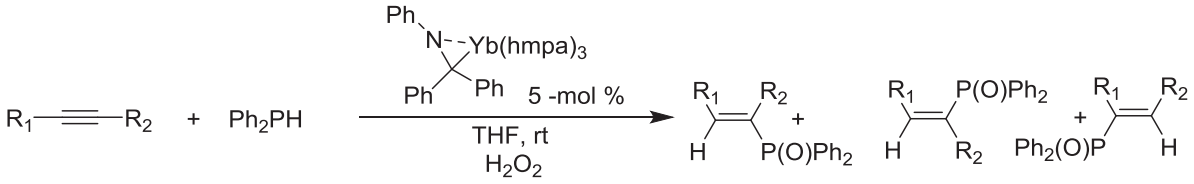
Scheme 1.16: Lanthanoide-catalyzed addition of phosphane to carbodiimides

MARKS showed that the catalytic intramolecular hydrophosphanylation/cyclization of phosphanoalkenes and phosphanoalkynes using organolanthanoide precatalyst of the type $Cp^*_2LnCH(TMS)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; Ln = La, Sm, Y; TMS = $SiMe_3$) and $Me_2Si(Me_4C_5)$(*t*-BuN)-$SmN(TMS)_2$ is thermodynamically possible. Thermodynamic investigations of lanthanoide catalyzed hydrophosphanylation/cyclization predicted that the insertion step is approximately energy-neutral (+2 kcal/mol) for alkenes and exothermic (-33 kcal/mol) for alkynes. The subsequent protonolysis step was exothermic for both alkenes (-17 kcal/mol) and alkynes (-7 kcal/mol) yielding the desired products after optimizing the further reactions conditions like light or temperatures to avoid the side reaction.[70] In total picture primary phosphanes were more reactive than the secondary phosphanes, most likely due to the different steric factors. The insertion of unsaturated carbon-carbon bonds into the Ln-P bond is believed to be the turnover limiting step in the catalytic cycle. Subsequently, the cycle is closed by a rapid protonolysis of the Ln-C bond to give the desired product as shown in **Scheme 1.17**.[70b, 71]



Scheme 1.17: Lanthanoide-catalyzed hydrophosphanylation/cyclization of alkenyl- and alkynylphosphanes.[70a]

In comparison to the mechanism shown in **Scheme 1.17**, in which the hydrophosphanylation occurs via an intramolecular reaction, the lanthanides La, Sm, Y and Yb catalyze an intermolecular hydrophosphanylation of alkynes with the assistance of imines generating non-cyclic alkenylphosphanes (**Scheme 1.18**).[72]



Scheme 1.18: Ytterbium-catalyzed intermolecular hydrophosphanylation of alkynes.

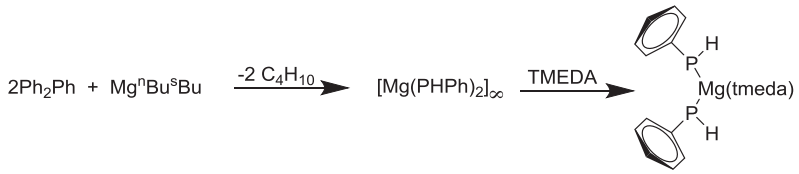
In a recently reported hydrophosphanylation of butadiene with PH_3 catalyzed by Cp_2EuH, the active species was proposed to be the phosphanido complex Cp_2EuPH_2.[73] This complex can be formed in two ways, either by a single-step reaction, corresponding to a P-H activation of PH_3 in the presence of Cp_2EuH, or by a two-step reaction, involving a 1,3-butadiene insertion (mainly a 1,4- insertion) into the Eu-H bond followed by a P-H activation. P-C bond formation occurs by insertion of C-C unsaturated bonds of the butadiene into the Eu-P bond.[73] Based upon these findings, early transition metals, late transition metals and lanthanoides showed effectiveness and high productivity in catalyzing the H-P/H-P(O) addition across unsaturated systems (such as alkynes, alkenes or carbodiimides) to produce

the desired products showing remarkable regio-, chemo-, and stereoselectivities as well as asymmetrical and symmetrical structures. In addition to these advantages of the lanthanoides as well as the early and late transitions metals, the application of them has also disadvantages like the toxicity of lanthanides, the difficulty of isolating or obtaining most of them and the high price. Therefore, the attention of researchers was to find alternative metals that can give nearly the same advantages, but with less disadvantages. Obviously, the s-block metals (groups I and II) are excellent candidates to pursue these aims, especially the calcium and strontium whose ionic radii are similar to those of Yb^{2+}[74] and Eu^{2+}[75], respectively.

1.3.3 Alkaline earth metal catalyzed H-P/H-P(O) addition

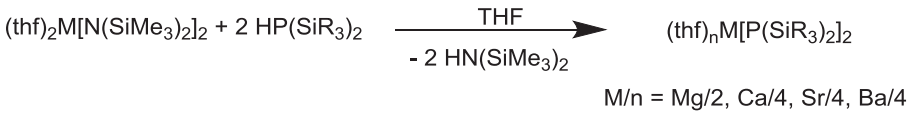
Substitution of the expensive transition metals and lanthanoides by calcium would allow a more economic catalysis, even though lower turnover numbers (TON) would be achieved. This strategy is supported by the fact that ytterbium(II) shows far reaching similarities to the heavy alkaline earth metal cations. Ytterbium(II)-mediated hydrophosphoranylation of alkynes[76] does not involve a change of the oxidation state of Yb(II) and a similar reaction behavior of calcium(II) and ytterbium(II) compounds seems possible. Additionally, group II elements possess many features which made them attractive metals such as global abundance, low toxicity and costs. Thus, the use of group II metals in place of the rare elements is desirable. Chemically, group II elements have lower electronegativity, a stable oxidation state of (+2), lack of redox reactions and the presence of various coordination sites because of the large ionic radii. These properties allow the use of the alkaline earth metals (especially calcium) in numerous areas such as preparation of calciumphosphanide. In 1942 the first alkaline earth metal phosphanides were reported by *LIGOUX*.[77] *LIGOUX* prepared an alkaline earth-*bis*-(phosphanide) via reacting of calcium or strontium with phosphane in liquid ammonia. Twenty years later, *Issleib* and *DEYLING*[78] were able to synthesize magnesium-*bis*-(diphenylphosphanide) by the metalation reaction of diphenylmagnesium and diphenylphosphane. *MASTHOFF* et al. isolated the heteroleptic $(Ph_2P)CaCl$ in 1969 through deprotonation of diphenylphosphane with $(Ph_3C)CaCl(thf)_2$.[79] In 1987, *HEY* et al.[80] prepared the monomer $Mg[P(H)Ph]_2(tmeda)$ from the reaction of the polymer

magnesium-*bis*-(phenylphosphanide) with *N,N,N′,N′*-tetramethylethylenediamine as shown in **Scheme 1.19**.



Scheme 1.19: Preparation of $Mg[P(H)Ph]_2(tmeda)$.[80]

In the 90s of the last century, *WESTERHAUSEN* isolated the complexes M-*bis*-(*bis*[trimethylsilyl]phosphanide) (M = Ca, Sr, Ba) via deprotonation of $HP(SiMe_3)_2$ with M-*bis*-(bis[trimethylsilyl]amides) as depicted in **Scheme 1.20**.[81]



Scheme 1.20: Synthesis of alkaline earth phosphanides.[81a]

In 1998 *KARSCH* and *REISKY* reported the synthesis of the complex $[(Me_2P)_2C(SiMe_3)]_2Ca(thf)_3$ in which the central calcium has a coordination number of 7, because the calcium atom coordinates with both of the phosphane donors of the bidentate ligand.[82] Few years later *IZOD* et al. prepared a series of complexes of heavy alkaline earth metals via the reaction the CaI_2, SrI_2 and BaI_2 with $K[P(CH\{SiMe_3\}_2)(C_6H_4\text{-}2\text{-}OMe)]$[83], where this anionic ligand forms a chelate of a five- membered ring with the alkaline earth metal. Indeed, an ether cleavage often accompanies the formation of such complexes and *IZOD* et al. showed that it is the case of the calcium as we can see in (**Figure 1.1**) while the ether cleavage was not observed in the cases of strontium and barium and the desired complexes could be isolated and characterized.[84]

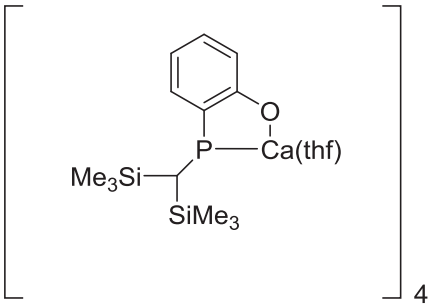
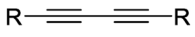
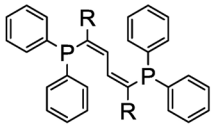
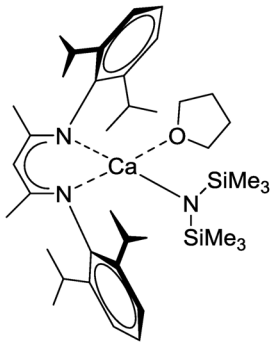
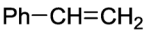
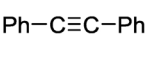
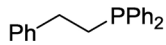
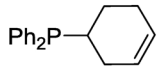
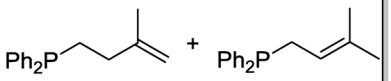
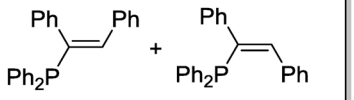
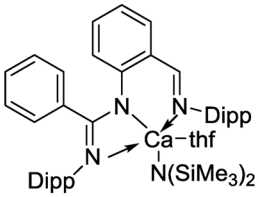
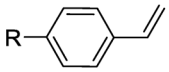
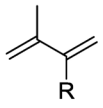
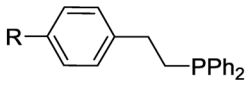
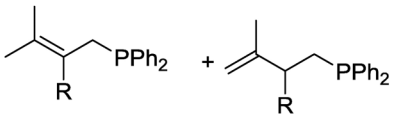
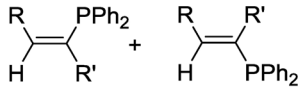


Figure 1.1: Products of the ether cleavages for the calcium case.[83, 85]

A similar result to that reported by *IZOD* from the reaction between alkaline earth metal(II) iodide with K[P(CH{SiMe$_3$}$_2$)(C$_6$H$_4$-2-NMe$_2$)] was obtained giving alkaline earth metal phosphanide complexes.[86] Shortly after that, *Hill* and coworkers[50] synthesized the heteroleptic calcium-diphenylphosphanide complex, [CH{C(Me)N-Dipp}$_2$]Ca(PPh$_2$)(thf), which is an intermediate in the hydrophosphanylation reactions catalyzed by the calcium β-diketiminato [{HC(C(Me)N-2,6-^{i}-Pr$_2$C$_6$H$_3$)$_2$}Ca{N(SiMe$_3$)$_2$}(thf)] complex. Calcium-, barium- and strontium-diphenylphosphanide complexes were successfully synthesized and characterized by *WESTERHAUSEN* and coworkers.[85] They showed that calcium did not possess the capability to deprotonate the secondary phosphane (HPPh$_2$). Therefore, two alternative reaction pathways allowed the synthesis of (thf)$_4$Ca(PPh$_2$)$_2$, either the salt metathesis reaction of CaI$_2$ with KPPh$_2$ (due to the insolubility of KI in THF), or the metallation of diphenylphosphane with (thf)$_4$Ca(Ph)PPh$_2$ or (thf)$_2$Ca[N(SiMe$_3$)$_2$]$_2$. On the other hand, the deprotonation of HPP$_2$ was accessible by metallic barium and strontium yielding barium and strontium-*bis*-(diphenylphosphanide) complexes. In 2007, *HILL* and coworkers[50] demonstrated that phosphaguanidines could be synthesized in high yield by the alkaline earth metal-catalyzed hydrophosphanylation of carbodiimides. A series of heavier alkaline earth metal-based catalysts including the heteroleptic calcium amide and the homoleptic alkaline earth amides [Ca{N(SiMe$_3$)$_2$}$_2$]$_2$, [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$], [Sr{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] and [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] were applied to the hydrophosphanylation of carbodiimides with diphenylphosphane, di-*p*-tolylphosphane and dicyclohexylphosphane.[87] In 2012 the first alkaline earth metallocene complexes carrying phosphanocyclopentadienyl ligands [M(L)$_x$(η^5-C$_5$H$_4$PPh$_2$)$_2$] (M = Ca, Sr or Ba, L = THF or

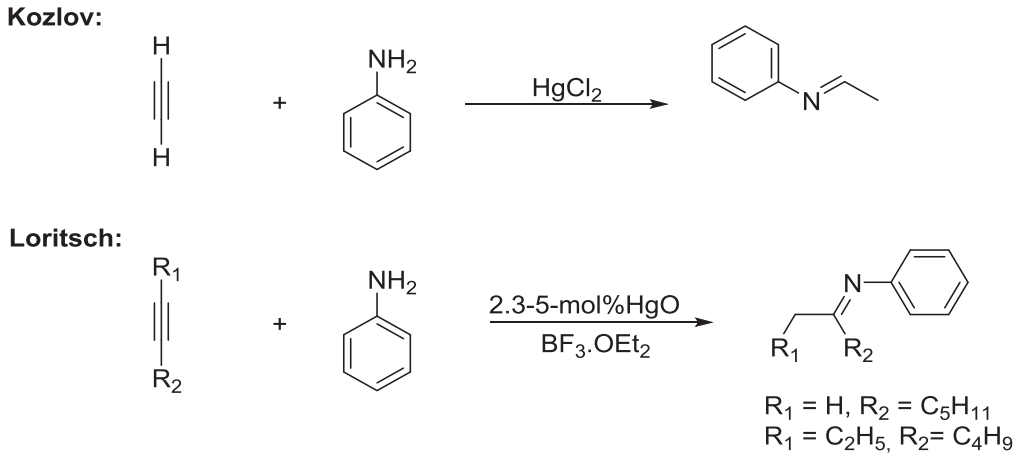
dme and x= 1 or 2) have been prepared by redox transmetallation/ protolysis reactions.[88] Most of the calcium phosphanide complexes, alkaline earth-phosphanide complexes, calcium-β-diketiminate and its derivatives or calcium-β-diketamidinate[{2-NC(Ph)NArC_6H_4CHNAr}Ca{N($SiMe_3$)$_2$}(thf)]$_x$, were applied as catalysts to accomplish hydrophosphanylation and hydrophosphoranylation reactions.[7d, 89] In **Table 1** we can see selected examples of calcium-phosphanide/-amide complexes catalyzing H-PPh_2 addition to alkynes and alkenes.

Table 1: Calciumphosphanide/-amide-catalyzed $HPPh_2$ addition to alkyne and alkene.[49b, 51b, 85, 90]

Catalyst	Substrate	Product(s)
$(thf)_4Ca(PPh_2)_2$	 R = Ph, $SiMe_3$, Mes, *t*-Bu, Me	
	 Cyclohexadiene isoprene 	   
	 R = H, Me  R = H, Me  R = Ph R'= H, Me,Ph, $SiMe_3$, ^nBu	 R = H, Me  R = H, Me 

1.4 Hydroamination

The addition of an amine N-H moiety across an unsaturated carbon-carbon linkage of alkenes, allenes or alkynes is termed as hydroamination. Formation of amides is a fundamental reaction in organic syntheses.[91] The importance of amides in biology, chemistry and technology is well recognized due to the presence of this functionality in many natural products, proteins, pharmaceuticals, and therapeutic drugs.[92] Organonitrogen compounds which are accessible via hydroamination reactions are widely encountered in industrial and natural products or synthetic drugs such as: Bactericides, herbicides, corrosion inhibitors, extraction agents, intermediates in the synthesis of penicillin, softening agents, wetting agents, dye fixers, asphalt emulsifiers, pigment dispersing agents, petroleum additives, a polymer in paper making, textile finishing.[93] Recently, it is reported that during the course of drug discovery almost 16% of all reported reactions are amide bond formation and over 50% of all drug candidates contain at least one amide bond functionality.[93] For example monomprine is one of the first natural products that became accessible by synthetic steps including a hydroamination step.[94] Moreover, the Chinese folk medicine uses organonitrogen compounds to treat cold, stomachache and rheumatism by extracts of the plant *Carduus crispus.* After extraction and characterization, the active materials of this plant were also synthesized in order to be used as inhibitors for some growing human cancer cells.[95] Indeed, hydroamination was one of the synthetic steps toward these active components of *Carduus crispus*.[95] Historically, hydroamination has got great attention owing to its important applications in various areas as mentioned above. In 1936 *KOZLOV* reported the first hydroamination reaction and the homogeneous catalyst mercury(II) chloride was used. *KOZLOV* described that the addition of aniline to acetylene in the presence of mercury(II) chloride leads to *N*-[(1*E*)-ethylidene]-aniline (**Scheme 1.21**, top).[96] Three years later, *LORITSCH* et al developed a mercury oxide catalyzed hydroamination of terminal and internal alkynes with aniline (**Scheme 1.21**, bottom).[97]

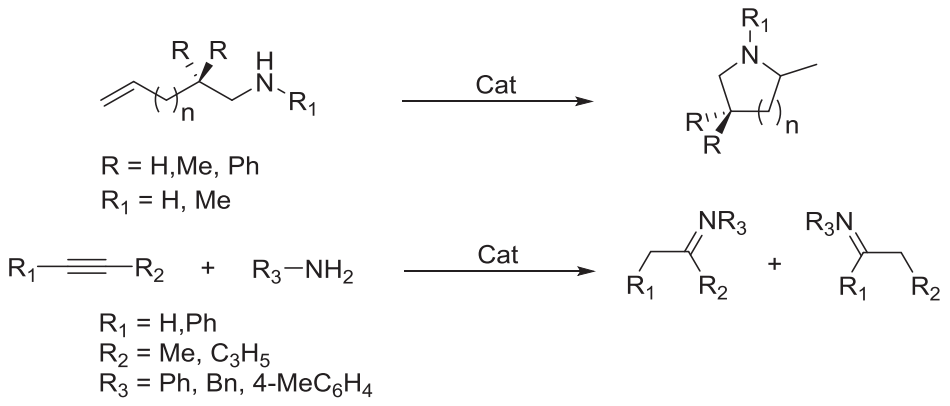


Scheme 1.21: First example of the hydroamination reaction catalyzed by mercury chloride/ oxide.[96-97]

Hydroamination has been examined with a variety of primary and secondary amines, cyclic and acyclic amines as well as anilines with diverse steric and electronic substituents. In addition to the type of the amine, the nature of the catalyst (homo-/heteroleptic) and the unsaturated system also influence the selectivity (regio-, chemo-, stereo-) of the reaction as well as the product symmetry (symmetrical or asymmetrical). The need of a catalyst is owing to the repulsive interaction between the amine lone pair and the electron-density of the unsaturated bond that makes the hydroamination a kinetically unfavorable process. Vastly, numerous catalysts have been prepared applying different methods such as: (i) direct metallation, (ii) salt metathesis, (iii) deprotonation (acid-base reaction). Catalysts based on metals throughout the periodic table have been reported using early and late transition metals,[98] lanthanoides and actinoides,[70b, 99] alkaline earth metals[49b, 87], and alkali metals which have been reported by *WEGLER and PIEPER* since 70 years.[100] Noteworthy hydroamination reaction can also be substantially accelerated by addition of catalytic amounts of acids [101] or bases [6, 102]. Furthermore, the presence of acid not only accelerates the reaction, but also it did enhance the enantioselectivity. Recently, *DONG* and coworkers have shown that the presence of *m*-xylylic acid leads to an enantioselectivity up to 90% ee.[103] The unsaturated substrates that have been investigated for intermolecular hydroamination reactions include alkenes, dienes, alkynes and allenes. For intramolecular hydroamination, various aminoalkenes and aminoalkynes have been examined.

1.4.1 Early and late transition metal-catalyzed hydroamination

Strikingly upon, hydroamination reactions have to overcome certain challenges such as unfavorable entropic effects, electrostatic repulsion between a strongly Lewis basic amine and an electron-rich multiple bond and lack of significant exothermic reaction enthalpy. Due to these facts, several strategies have been developed to support the addition of N-H functionalities to the C-C multiple bonds. On the one hand, activation of alkenes and alkynes often succeeds in the vicinity of late transition metals by back-donation of charge from the metal-centered d orbitals into π* orbitals of the alkenes and alkynes, in agreement with the *Dewar-Chatt-Duncanson* model.[104] On the other hand, the amines can be activated by oxidative addition to transition-metal complexes or by deprotonation and formation of the much more aggressive and nucleophilic amides (R_2N^-) or even imides (RN_2^-) of early transition metals or s-block metals. The disadvantageous entropy value can be minimized by an intramolecular hydroamination reaction, leading to cyclic amines or imines. Organoreset complexes of early transition metals such as group IV have been used to catalyze the inter- and intramolecular hydroamination reactions. The application of group IV metal complexes to intramolecular alkene hydroamination has become a vibrant and quickly developing field since the first reports have been published.[12, 105] Comparing the complexes of group IV elements and those of the rare earth and alkaline earth metals will lead to several important features of these catalysts: (i) the reactivity of group IV metal catalysts remains low, thus demanding higher catalyst loading and temperatures, which often leads to side reactions. (ii) Generally catalysts of group IV are restricted to *gem*-dialkyl-activated substrates and terminal alkene moieties. (iii) Only few systems are able to approach cyclization of both primary and secondary aminoalkenes and aminoalkynes.[7b, 106] Homoleptic amides of titanium[105b] and zirconium[107] have been used as catalysts for the cyclization of aminoalkenes (**Scheme 1.22**, top). In numerous cases, titanium catalysts are significantly more reactive than zirconium or hafnium catalysts not only in intramolecular hydroamination of aminoalkenes, but also intermolecular hydroamination of asymmetric, symmetric, internal and terminal alkynes as we can see on the bottom of **Scheme 1.22**.



Scheme 1.22: Group IV catalyzed intramolecular and intermolecular hydroamination of alkenes and alkynes.[105b, 106b, 107-108]

Group V metal complexes have been also used to catalyze hydroamination reactions as recently was reported by *HULTZSCH* and coworkers.[109] They could show that group V complexes are more active than group IV to obtain the asymmetric products which are results from hydroamination reactions of aminoalkenes as well as alkenes, which is catalyzed by binaphtholate tantalum and niobium derivation (**Figure 1.2**, left).[109] The chiral complex vanadium(IV)-*bis*-(amidate) (**Figure 1.2**, right) also showed appreciable catalytic activity and enantioselectivity for the asymmetric hydroamination/cyclization whereas the corresponding tantalum complex was not an efficient catalyst.[13]

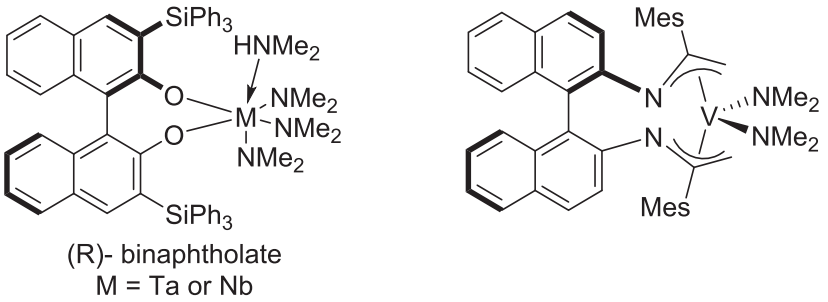


Figure 1.2: Selected group V metal catalysts for asymmetric hydroamination.[13, 109]

Complexes of late transition metals are highly desirable for catalytic hydroamination due to their low reactivity toward oxygen-containing functional groups. Many different catalyst systems of the late transition metals have been disclosed and developed within the past

decade and showed high efficiency. **Figure 1.3** represents an overview of various late transition metal-based catalysts. Gold[110] and silver[111] complexes have been deeply and intensively studied for the hydroamination of unsaturated systems such as alkenes, allenes, and alkynes. Silver and gold catalysts are often combined to catalyze hydroamination reactions, whereas silver salts with non-coordinating anions are used to abstract halide ions from gold catalyst and thereby to enhance its Lewis acidity. In addition, gold complexes are of particular efficiency for catalyzing the asymmetric addition reactions (for example, intermolecular hydroamination of 1,3-dienes and allenes). Furthermore, gold catalysts have been reported to give extremely high turnover numbers up to 9500.[112] Palladium complexes are intensively used in both types of hydroamination reactions to hydroaminate alkynes or aminoalkynes. For instance, intramolecular hydroaminations of aminoalkynes represent an advantageous strategy to synthesize indoles.[113] Additionally, palladium is the ideal metal for C-C coupling / intramolecular hydroaminations. Nonetheless, the intermediate alkyl-palladium tends to undergo β-hydride eliminations and hence limits the use of Pd in intermolecular hydroaminations of alkenes. However, this fact opens new opportunities for oxidative amination processes. In contrast, platinum complexes have low tendency toward β-hydride eliminations. Therefore, they show high efficiency to accomplish intra- and intermolecular hydroamination of alkynes and alkenes.[114] In relation to late transition metal-catalyzed hydroamination reactions, rhodium complexes have been reported as excellent active catalysts in intermolecular hydroamination of not only alkynes, but also alkenes in addition to their high selectivity for *anti*-Markovnikov addition products.[115] In assistance of chiral 2-dialkylphosphano-2´-alkoxy-1,1-binaphthyl ligands, Rh allows an efficient synthesis of various chiral amines via asymmetric cyclization of aminoalkenes.[116] Similar to Rh, iridium complexes are active in both types of hydroamination of terminal alkynes and alkenes with anilines and heteroaromatic amines, but in counter to Rh, hydroamination reactions catalyzed by Ir usually lead to Markovnikov addition products.[117] Moreover, chiral Ir complexes have been also reported as efficient catalysts to accomplish the asymmetric intermolecular hydroamination of alkenes with heteroaromatic amines.[118] Ru catalysts are basic catalysts for the hydroamination of terminal alkynes with highly regio- and stereoselectivity. These catalysts also show high efficiency in asymmetric intermolecular hydroaminations of alkenes.[119] As rival of ruthenium, Re catalysts have been

recently reported as active catalysts to hydroaminate terminal alkynes that are usually catalyzed by Ru catalysts.[120] Nevertheless, for industrial purposes not only an efficient catalysis is required, but also inexpensive catalysts. Thus, transition metals such as Fe, Co, Ni, and Cu are still highly favorable for designing catalysts for hydroamination reactions. Iron has been engaged to catalyze intramolecular hydroamination of allenes, alkenes and alkynes. Cobalt has been described as an excellent catalyst in formation of C-N bonds via the reactions of hydrazines and azides as *CARREIRA* et al. reported in 2004 and 2005.[121] Nickel complexes have been reported to promote intermolecular hydroamination of alkynes, 1,3-dienes and some activated alkenes with aliphatic amines, but under harsh conditions of high catalyst loading and refluxing.[122]

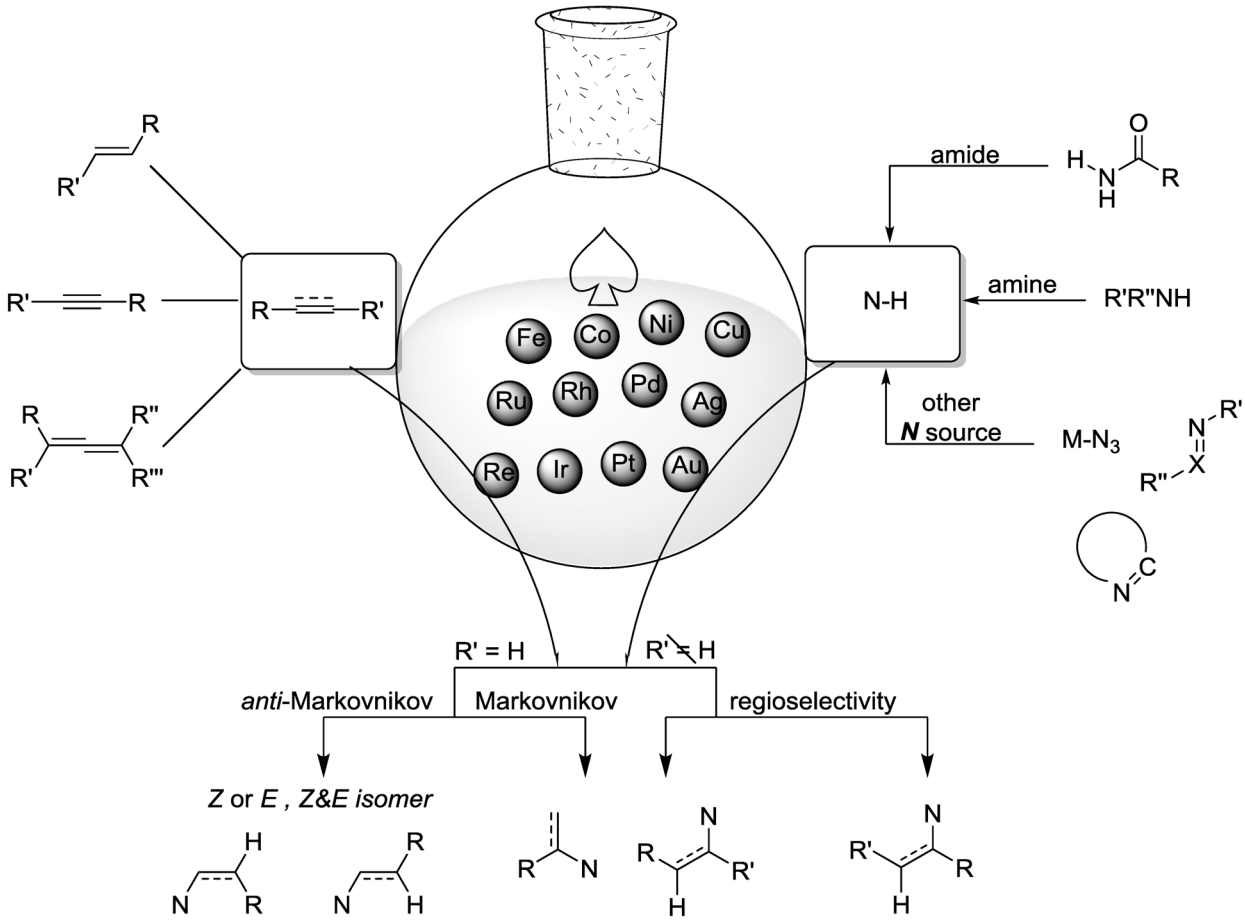
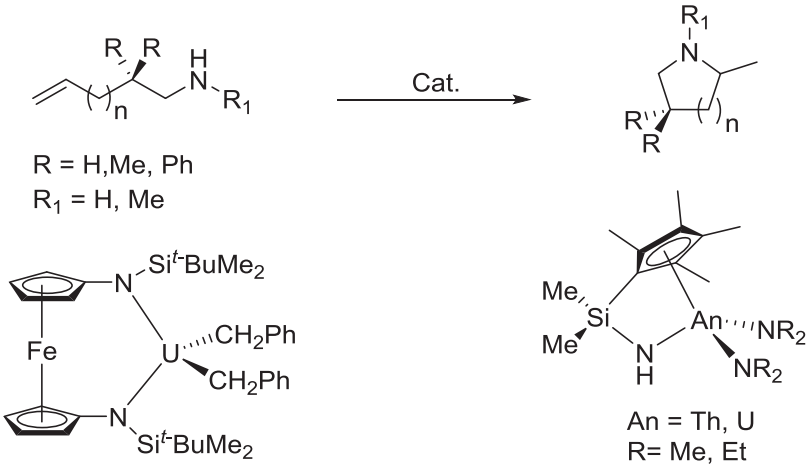


Figure 1.3: Reaction pathways and product types in N-H addition reactions catalyzed by late transition metal complexes.

1.4.2 Lanthanoides and actinoides catalyzed hydroamination

Similar to the addition of H-P moieties across unsaturated systems, rare earth metal complexes have proven to be very active and efficient catalysts for H-N addition across unsaturated linkages. In comparison with organolanthanoide[123] catalysts, only a limited number of organoactinoide catalysts has been investigated for inter-/intramolecular hydroamination reactions.[124] Although organoactinide catalysts showed in many cases higher efficiency and wider application for a broad range of substrates [124a-c] than the corresponding organolanthanoide catalysts, their use is limited because of many factors related to the costs, lack of global abundance and health risks as well as difficulties of dealing with these metals. For example, the thorium and uranium complexes (**Scheme 1.23**, bottom right) show higher activity to catalyze the intramolecular hydroamination reaction than the corresponding organolanthanoide complexes. Also one of the important actinoide complexes, which is used as catalyst for the hydroamination of aminoalkenes, is the ferrocene diamido-uranium complex as shown in **Scheme 1.23**, bottom left.

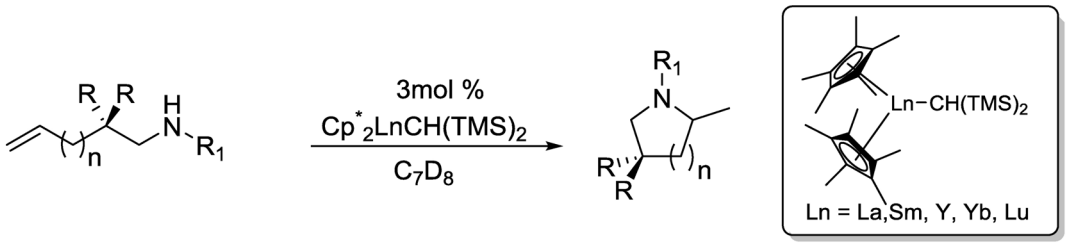


Scheme 1.23: Organoactinides complexes catalyzed hydroamination reaction.[124a-c]

Despite the difficulties in intermolecular hydroamination reactions catalyzed by organolanthanides complexes that are caused by the inefficient competition between strongly binding amines and weakly binding alkenes for available coordination sites at the catalytically active center, some examples have been reported.[125] On the other hand complexes of organolanthanoides are very efficiently in catalyzing intramolecular

hydroamination reactions. A various number of catalyst systems of organolanthanoides has been developed over the last decade and these systems can be divided into two types:

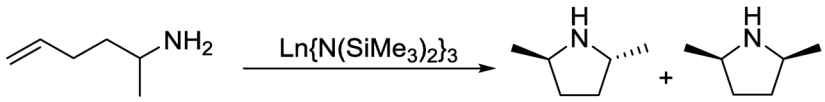
(i) Cyclopentadienyl lanthanoide- (or half sandwich and lanthanocenes) based catalyst systems: The catalyst systems $Cp^*_2LnCH(TMS)_2$ showed high efficiency toward catalyzing the intramolecular hydroamination of terminal aminoalkene systems to afford 5-, 6- and 7-membered ring products as shown in **Scheme 1.24**.[126] It has also been observed that the formation of the 5-membered ring is faster than that of the 6- or 7- membered rings in the presence of *gem*-dialkyl substituents. Moreover, the cyclization rate becomes higher with increasing ionic metal radii.[126-127]



Scheme 1.24: Lanthanocene-catalyzed intramolecular hydroamination of terminal aminoalkenes.[126]

Regardless of abovementioned advantages of lanthanocene, these catalysts suffer from air and moisture sensitivities in addition to that they are not commercially available.

(ii) Cyclopentadienyl free lanthanides catalysts: Several catalysts containing chelating diamines, such as $Ln[N(TMS)_2]_3$[99c, 128] have shown good activity in intramolecular hydroamination and accomplished the cyclization of the chiral aminoalkenes with high diasteroselectivity [99d] as it is shown in **Scheme 1.25**.



Scheme 1.25: Diastereoselective cyclization of chiral aminoalkenes.[128a, 129]

This highly diasteroselective hydroamination have been used in many syntheses such as preparation of (±)-xenovenine.[130] Many other similar organolanthanides have been also reported as efficient catalysts such as trisamides,[90, 99c, 128b] *bis*-amide complex

$Sm\{N(SiMe_3)_2\}_2$[131] or chelating diamides,[99c, 99d, 129] diamidoalkylamine complexes,[128a] amino troponiminato,[132] *bis*-(phosphanimino)- methanide,[133] salicylaldiminato[9, 134] and β-diketiminate. Complexes of β-diketiminate can be synthesized with good yields by the transmetallation reaction as has been reported for samarium and gadolinium β-diketiminate complexes by *DREES* et al..[135] Similarly complexes of cesium, samarium and neodymium β-diketiminate were described by *HITCHCOCK* et al..[136] The lanthanide complexes with β-diketiminate ion could also be chargeable systems in special cases, for example the β-diketiminato scandium complex, has been reported by *LAUTERWASSER* et al., is cationic (**Figure1.4**).[9] This cationic system did show improved catalytic activity over its neutral congener.

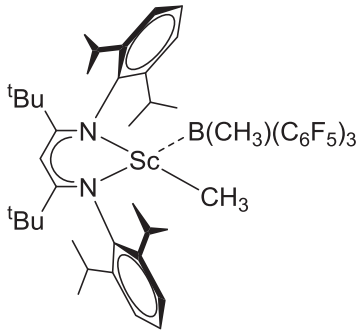


Figure 1.4: cationic β-diketiminateo scandium complex.

1.4.3 Alkaline metal-catalyzed hydroamination

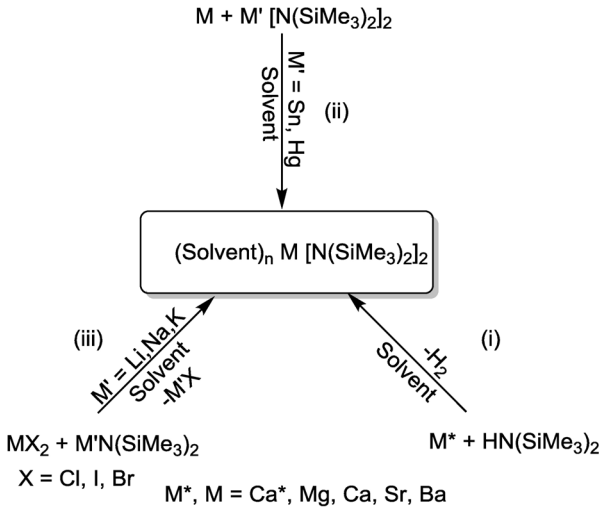
Alkaline metals such as Li, Na, k and Cs have been used as strong base or strong electropositive metals to catalyze hydroamination reactions for a long time.[6a, 102] Lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), lithium diethylamide-tetramethylethylendiamine ($LiNEt_2$-TMEDA) and lithium tetramethylpiperidide (LiTMP),[137] as well as *n*-BuLi[138] and *sec*-BuLi[138c] are widely employed to deprotonate various substrates and to catalyze inter-/intramolecular hydroamination reactions. Na metal has been reported to mediate hydroamination reactions, like the addition of aniline to 1,3-butadiene at high temperature,[139] while the use of organosodium complexes such as sodium

naphthalenide (Na_2Naph) or sodium ethoxide (NaOEt) as a catalyst were sufficient to accomplish hydroamination reactions at room temperature.[140] To the best of our knowledge pure potassium has never been used successfully as a catalyst for hydroamination reactions, but organopotassium compounds have been studied. For example, KO-*t*-Bu has been used as a catalyst for the addition of primary and secondary amines to unsaturated systems.[141] In addition, K_2CO_3 has also been used for the same desires.[142] Caesium hydroxide ($CsOH.H_2O$) solution has been reported as a catalyst for hydroamination reactions in the beginning of this century.[143] However, this compound is not commonly used as a catalyst because the extraction process of caesium compounds is very expensive and these compounds behave very much like rubidium hydroxide and potassium hydroxide even though they are more reactive. Moreover, organo alkali metal compounds have been employed to enhance the activity and the efficiency of other transition metal catalytic systems. For example *n*-BuLi[144] and $CsNH_2$/$RbNH_2$[143] have been used as cocatalyst to promote Co[acac].

1.4.4 Alkaline earth metal-catalyzed hydroamination

Although organolanthanoide catalysts possess surpassed reactivity in inter-/intramolecular hydroamination, the development of more robust, environmentally benign and readily available catalysts remains an important target. Due to the fact that many of the lanthanoides are similar to alkaline earth metals, for example Ca and Sr to Yb(II)[74] and Eu(II),[75] respectively. There is a growing interest in the syntheses and characterization of group II-amides due to their utility as a precursor for the synthesis of a spectrum of group II compounds [7d, 52b, 145] and also as versatile catalysts in various organic transformations.[7d, 50, 146] This interest has been begun in the 60s of last century when *JUZA* et al. recognized that strontium and barium in liquid ammonia can form the corresponding amides, $Sr(NH_2)_2$[147] and $Ba(NH_2)_2$[148] within some days, while calcium required more than one month to react with liquid ammonia[147] and the synthesis of magnesium-*bis*-amide was successful via reacting magnesium nitride with ammonia under harsh conditions (350 °C, 10 bar).[149] A few years later *UTKE* and *SANDERSON*[150] were able to synthesize many calcium amide complexes, which are sensitive to the air and moisture as well as poorly soluble and pyrophoric, via reacting different amines with the solvated calcium in ammonia. Metalation

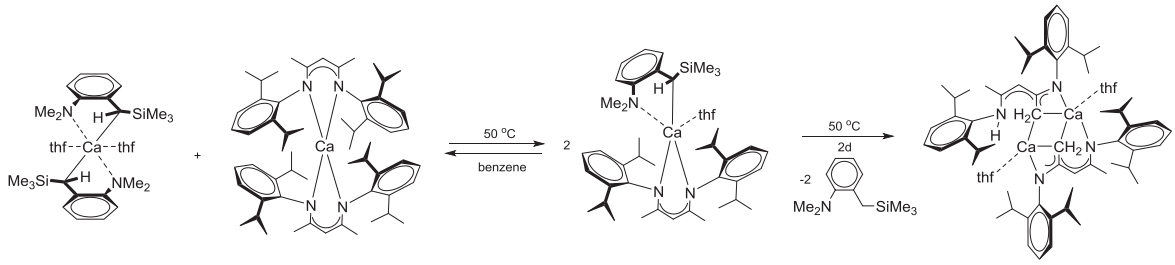
reactions allowed *ISSLEIB* and *DEYLING*[78] in 1964 to prepare Mg-*bis*-[diphenyl amide] via reacting diphenyl amine with diethyl magnesium. In 1975 *FRÖHLICH* was able to prepare the following complexes: Mg-, Ca-, Sr-, Ba-*bis*-[diphenylamide] coordinated with 1,4-dioxane, which have been prepared via employing metathesis reaction of Ca-, Sr-, and Ba-iodide/ Mg bromide with potassium diphenyl amide.[151] In the 90's of the last century remarkable amides with better solubility in organic solvents have been prepared by *WESTERHAUSEN* and characterized with different spectroscopic technique. Due to the fact that calcium metal in liquid ammonia does not react with hexamethyldisilazane even after addition of mercuric chloride as a catalyst.[81, 152] Therefore, he prepared the calcium and homologous of alkaline earth metal hexamethyldisilazanides (alkaline earth metal-*bis*[bis(trialkylsilyl)amides]) coordinate with ethers (the reaction solvent) like tetrahydrofuran or dimethoxyethane by the following reaction ways: direct metallation (i), transmetallation (ii), or salt metathesis (iii) reaction as shown in **Scheme 1.26**.[81, 152-153]



Scheme 1.26: Synthesis of *bis*-[*bis*-(trimethylsilyl)amides] of the alkaline-earth metals.

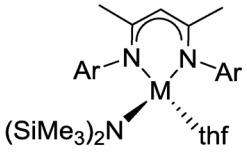
HILL and coworkers showed that $[Sr\{N(SiMe_3)_2\}_2]_2$ acted as precatalyst for the hydroamination of diphenylacetylene with piperidine. However, attempts to perform hydroamination with aniline under similar conditions were unsuccessful due to low nucleophilicity and solubility issues.[154] Calcium-based hydroaminations are extremely attractive because calcium is nontoxic, easily available and inexpensive. Furthermore, Ca combines s-block metal behavior (strongly heteropolar bonds, salt-like behavior) with the

properties of early transition metals and divalent lanthanides (d-orbital participation, catalytic activity). However, one major problem in studying the catalytic features of Ca-compounds is related to the solubility and therefore many efforts have been made in order to enhance the solubility, but this leads to decreased reactivity. As an example, calcium-*bis*[*bis*(trimethylsilyl)amides] are soluble in common organic solvents, but the reactive Ca-N bonds are effectively shielded and the reactivity is reduced.[81a] Large and/or multidentate ligands can circumvent this solubility issue. It has been found that heteroleptic calcium *β*-diketiminate complexes with bulky substituent complexes are highly soluble and possess sufficient reactivity to accomplish the intramolecular hydroamination of aminoalkenes. The chemistry of the ligand *β*-diketiminate has started in the middle to late 1960's as homoleptic complexes of Co, Ni, Cu, Zn[155] and lanthanoide elements.[135b, 136, 156] Based on the facts that there are direct parallels between the chemical behavior of the heavier alkaline earth metals and lanthanides, L (L = $CH(CMe\text{-}2,6\text{-}i Pr_2C_6H_3N)_2$) has stabilized the first example of a monomeric magnesium(I) compound $[LMg]_2$ with a Mg-Mg bond.[157] Furthermore, at the beginning of this century, *HARDER* represents another resemblance between the chemistry of alkaline earth and early d- and f-block metals by his observation of C-H activation in a benzylcalcium complex which acted as an initiator for the living syndiotactic polymerization of styrene.[158] Thus, the success of the *β*-diketiminate ligand in polymerization catalysis[159] promoted their use in heteroleptic benzylcalcium initiators. *HARDER* showed that these heteroleptic alkaline earth complexes can be prepared by ligand-exchange between two homoleptic compounds with the consideration of the steric and electronic effects as well as the thermodynamic and kinetic effects as shown in **Scheme 1.27**.[158a]



Scheme 1.27: Synthesis of heteroleptic calcium complexes by ligand exchange. [158a]

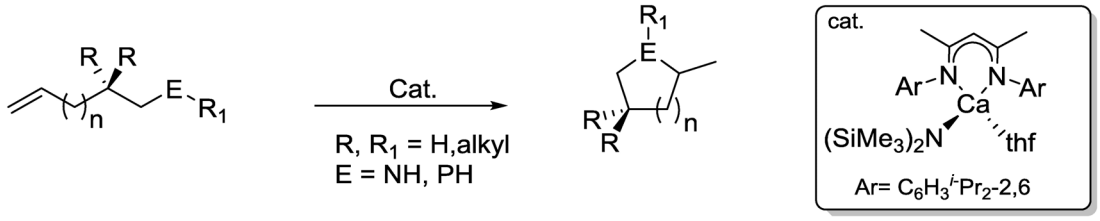
A few months later *CHISHOLM* [160] reported the reaction of the *β*-imino-enamine (HL) with two equivalents of potassium-*bis*(trimethylsilyl)amide and one equivalent of calcium-, strontium- , and barium-iodide to isolate the corresponding heteroleptic complexes [LM{N(SiMe$_3$)$_2$}(thf)] (M = Ca, Sr, Ba) as shown in **Figure 1.5**.



M= Ca, Sr, Ba
Ar= $C_6H_3{}^{i}Pr_2$-2,6

Figure 1.5: Heteroleptic complex of alkaline earth metals-*β*-diketiminate.[160]

HILL and coworkers studied the kinetics of the heteroleptic complexes [LM{N(SiMe$_3$)$_2$}(thf)] (M = Ca, Sr, Ba) and used them for the preparation of new materials by the exchange of the coordinated solvent molecule or by the exchanging of the hexamethyldisilazide anion. For example, the [LCa{N(SiMe$_3$)$_2$}(thf)] has been used to synthesize the heteroleptic calcium complexes [LCa{N(SiMe$_3$)$_2$}(NH$_2$Cy)], [LCa{N(SiMe$_3$)$_2$}(NH$_2{}^{t}$-Bu)], and [LCa{NH(2,6-*i*-Pr$_2$C$_6$H$_3$)}(thf)]. Furthermore, the centrosymmetric dimer [LCa{NHCH$_2$CH$_2$OCH$_3$}]$_2$ in which the five coordinate calcium centers are bridged by unsymmetrical Ca-N-Ca´ interactions has been prepared by the exchange of both coligands and this derivate is considered as the first example of a Ca complex having a coordination number of 5.[161] Additionally, heteroleptic calcium-*β*-diketiminate complexes have been used by *HARDER* and *HILL* to accomplish the challenging intramolecular hydrophosphanylation, hydrophosphorylation and hydroamination of various phosphanoalkenes, phosphoranoalkenes, and aminoalkenes as shown in **Scheme 1.28**.[49b]



Scheme 1.28: Intramolecular hydrophosphanylation, -phosphorylation and -amination reactions catalyzed by calcium-*β*-diketiminate complexes.[49b]

In consideration of the atomic radii of alkaline earth metals and their similarity to rare earth metals radii's and in order to tune the catalytic performance and reaction patterns of the complexes of these highly electropositive metals, in 2012 *CUI* and coworkers reported the synthesis of calcium-*β*-diketamidinate [{2-NC(Ph)NArC_6H_4CHNAr}Ca{$N(SiMe_3)_2$}(thf)] and the corresponding Yb complex that are stabilized by a tridentate ligand. These complexes showed higher efficiency and selectivity than the calcium-*β*-diketiminate in the intermolecular hydrophosphanylation reaction (**Table 1**).[90] *WESTERHAUSEN* and coworkers reported earlier that calcium-*bis*(diphenylphosphanide) acts as a catalyst to accomplish hydrophosphanylation reactions of diphenylphosphane across the C≡C triple bonds of different substituted butadiene backbones (**Table 1**).[51b] Similarly, calcium-*bis*-(diphenylamide) has been synthesized, characterized and used as catalyst to accomplish the addition of diphenylamine across C≡C triple bond of diphenylbutadiyne. It has been found that $Ca(NPh_2)_2$ is less active than $Ca(PPh_2)_2$ and not efficient enough to accomplish the amine addition. Hence, a reactivity enhancement research has been carried out and series of "ate" complexes could be synthesized via salt metathesis reactions, where excess amounts of potassium amide salts are necessary for the formation of the calciate complexes $[K_2Ca(NRAr)_4]_\infty$ (R= H, Ph, Me. Ar = Dipp, Ph) that were successfully synthesized and characterized.[162]

2 Motivation of this work

In industry, several important factors must be considered in determining any catalytic process such as the costs of substrates, atom efficiency and process economics. Despite the fact that hydroamination or hydrophosphanylation reactions proceed with 100% atom economy (without waste production) and the unsaturated carbon linkages, amines and phosphanes are most often economically advantageous compared to other starting materials for certain product, the main cost determining issue for these reactions is the catalyst cost.
Calcium represents one of the most attractive metal with respect to the future applications in chemistry due to the properties such as:

- Abundance (the fifth most frequent element in the earth's crust with 3.4 wt. %).[49b]
- Inexpensive compared to other metals like platinum or palladium (10€ per mol vs ~ 4500€ per mol).
- The non-toxicity of calcium containing solutions (regardless of its concentration) allows diverse applications in medicine and biomedicine as well as in the preparation of materials for surgery, orthopedics, and tissue engineering.
- **Calcium** has lower electronegativity compared to rare earth metals and its stable oxidation state of +II.
- Ability of Ca to be coordinated to various ligands due to its large ionic radius (1.06 Å).
- The intermediate position in the periodic table between typical s-block metals and early transition metals makes calcium a fascinating element because it combines d-orbital participation in bonding situations and catalytic activity with very heteropolar bonds of an enormous reactivity.

In this research work diphenylbutadiyne will be the only alkyne used here despite the fact that alkynes have more π-electrons than alkenes, which could be expected to increase the electrostatic repulsion of the nucleophile where metal-catalyzed addition reactions across C≡C triple bonds are much easier to occur than those across C-C double bonds. This can be explained by the formation of substantially weaker π-bonds between the metal center of most catalysts and alkynes as compared to alkenes. The intermediate strength of the interaction

between the alkyne and the catalyst allows activating the C≡C triple bond toward nucleophilic attack without inhibiting the reaction by a strong π-coordination to the metal center. Furthermore, alkynes are sterically less hindered toward attack of the nucleophile. In addition, hydroamination of alkynes yields either imines or enamines, which are useful reagents for a wide variety of organic transformations. The aims of this thesis are summarized by the following points:

(1) Synthesis and characterization of calcium and calciate catalysts which are capable to accomplish the addition of amines or phosphanes across the C≡C triple bonds of diphenylbutadiyne.

(2) Application of the synthesized catalyst to mediate the hydroamination of diphenylbutadiyne by primary amines.

(3) Hydroamination of diphenylbutadiyne by secondary amines and optimization of the regioselectivity.

(4) Studying the reactivity of the prepared catalysts toward the addition of diphenylphosphane across the singly hydroaminated diphenylbutadiyne.

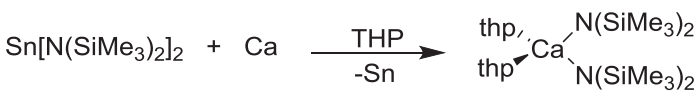
3 Results and Discussion

In this section all the achievements will be shown and scientifically discussed, starting from the synthesis of the efficient catalyst, followed by the reactivity study of these catalysts in the addition of various of primary and secondary arylamines to diphenylbutadiyne as well as the addition of diphenylphosphane to the singly hydroaminated products.

3.1 Synthesis and characterization of calcium and calciate complexes

3.1.1 Synthesis and structural characterization of $(thp)_2Ca[N(SiMe_3)_2]$ [**1**]

At the beginning of this work we were focusing in preparation of new calcium complexes which is enough active to mediate the addition of amines and phosphanes across a diyne system. Due to the tremendous importance of $[Ca\{N(SiMe_3)_2\}_2]$ as thf adduct in organocalcium chemistry, we applied it as catalyst to accomplish the addition of primary amine across diphenylbutadiyne, but the reactivity of this catalyst was not high enough. However, tetrahydrofuran exhibits ring strain and α-acidic hydrogen atoms and hence, ether cleavage can occur quite easily during metal-organic transformations. According to the fact, that tetrahydropyran (thp) is a weaker and bulkier base than thf, we expected that a slight enhancement in the reactivity could be gained. Therefore, we investigated the tetrahydropyran adduct of $[Ca\{N(SiMe_3)_2\}_2]$. In order to obtain halide-free $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ [**1**], we have chosen the transmetalation of freshly distilled $Sn[N\{SiMe_3\}_2]_2$ with calcium granules according to **Scheme 3.1**. During this heterogeneous reaction the color of the solution turned reddish brown. After filtration, removal of the solvent in vacuum and recrystallization of the residue from *n*-hexane, pure [**1**] was isolated as shown in **Figure 3.1**. Other preparative routes also seem to be feasible. However, considering the recent report from *JOHANS* et al.[163] the salt-metathesis reaction can yield $[Ca\{N(SiMe_3)_2\}_2]$ that is contaminated with $KN(SiMe_3)_2$.



Scheme 3.1: Synthesis of $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$.[164]

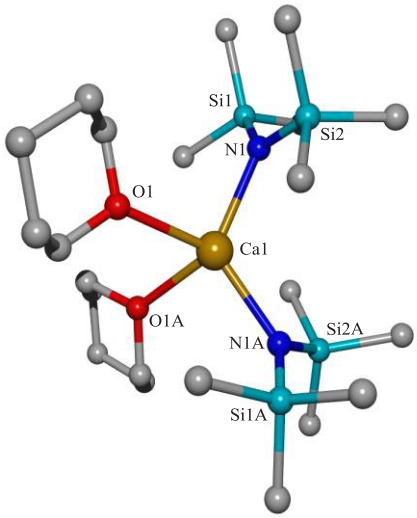


Figure 3.1: Molecular structure and numbering scheme of $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ [**1**]. The ellipsoids represent a probability of 40 %, H atoms are neglected for clarity reasons. Symmetry-related atoms (-x+1, y, -z+0.5) are marked with the letter "A". Selected bond lengths (pm): Ca1-N1 231.08(11), Ca1-O1 240.23(9), N1-Si1 168.84(11), N1-Si2 168.95(12), Ca1···C6 318.16(17), Ca1···Si1 346.56(4), Ca1···Si2 334.39(4); angles (deg.): N1-Ca1-N1A 119.43(6), N1-Ca1-O1 94.31(4), N1-Ca1-O1A 134.86(4), O1-Ca1-O1A 78.57(5), Ca1-N1-Si1 119.31(6), Ca1-N1-Si2 112.49(5), Si1-N1-Si2 128.19(7).

The tetra-coordinate metal atom is in a severely distorted tetrahedral coordination sphere with a large N1-Ca1-N1A angle of 119.4°. The nitrogen atoms are in distorted trigonal planar environments with an average N-Si bond of 168.9 pm. This short bond is characteristic for bis(trimethylsilyl)amides bound at electropositive s-block metals[165] because the hyperconjugation of the negative charge from the p_z(N) orbital into σ*(Si-C) orbitals strengthens the N-Si bonds. The bulkiness of the trimethylsilyl groups enforces a large Si1-N1-Si2 bond angle. In order to evaluate structural characteristics, mononuclear calcium-*bis*[bis(silyl)amides] are summarized in **Table 2**. The compounds are arranged according to the coordination number of the calcium atom [CN(Ca)] and within these groups according to the Ca-N distances. It is obvious that bulkier silyl substituents lead to elongated Ca-N bonds which vary between 227 and 239 pm. The Ca-L distances (the donor atoms are given in brackets) strongly depend on the donor base because the atomic radii decrease from C over N to O. However, the major influence of these co-ligands on the Ca-N bond lengths seems to be of steric nature. Even the coordination number of calcium plays a minor role as

can be seen from the complexes with three- and five-coordinate alkaline earth metal centers showing Ca-N values well within the range for adducts with tetra-coordinate calcium atoms.

Table 2: Comparison of selected structural parameters of mononuclear calcium *bis*[bis(silyl)amides] of the type [(L)Ca{$N(SiR_3)_2$}$_2$] [average values, bond lengths /pm and angles /°, CN(Ca) coordination number of calcium; dme 1,2-dimethoxyethane, thf, thp, *t*-BuIm *N*-tert-butylimidazole, tmeda tetramethylethylenediamine, py pyridine, dmap 4-dimethylaminopyridine, hmpa hexamethylphosphoric acid triamide].

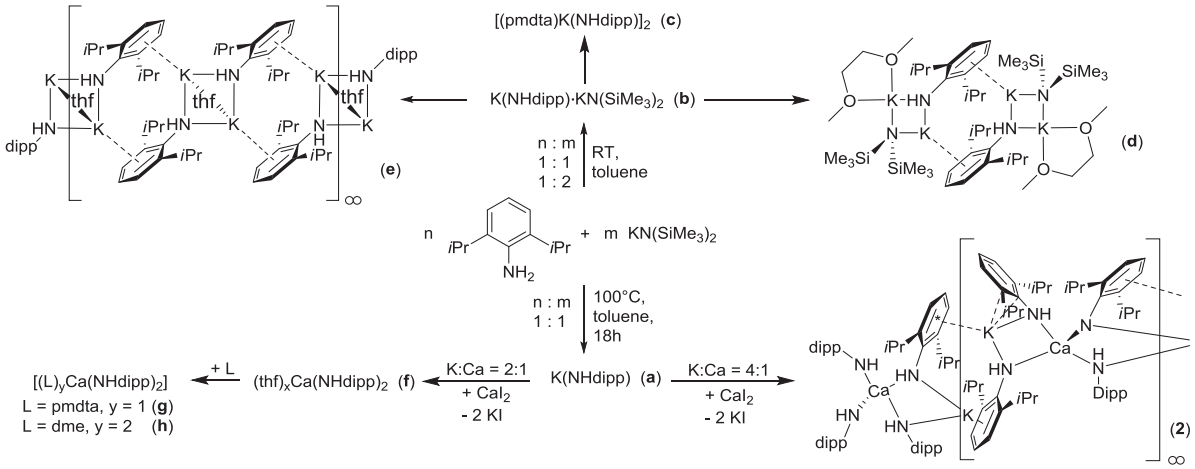
L	$NSiR_3$	CN(Ca)	Ca-N /pm	Ca-L /pm	N-Ca-N/°	Ref.
NHC-1	$N(SiMe_3)_2$	3	229.0	259.8 (C)	125.4	[166]
NHC-2	$N(SiMe_3)_2$	3	230.3	262.9 (C)	124.5	[166]
thf	$N(SiMe_3)(SiPh_2t\text{-Bu})$	3	232.3	238.2 (O)	134.6	[167]
dme	$N(SiMe_3)_2$	4	227.1	239.7 (O)	123.6	[168]
2 thf	$N(SiMe_3)_2$	4	230.2	237.7 (O)	121.3	[169]
2 thp	$N(SiMe_3)_2$	4	231.2	240.2 (O)	119.4	[164]
1 tmeda	$N(SiMe_3)_2$	4	231.5	259.2 (N)	121.8	[170]
2 *t*-BuIm	$N(SiMe_3)_2$	4	232.5	246.4 (N)	123.3	[171]
2 Ph_3PO	$N(SiMe_3)_2$	4	233.7	226.5 (O)	129.4	[166]
2 py	$N(SiMe_3)(SiMe_2t\text{-Bu})$	4	235.3	253.7 (N)	125.3	[167]
2 thf	$N(SiMe_3)(SiPh_3)$	4	236.0	237.3 (O)	146.6[a]	[167]
2 dmap	$N(SiMe_3)(SiMe_2t\text{Bu})$	4	236.7	249.8 (N)	122.3	[167]
2 hmpa	$N(SiMe_3)(SiMe_2t\text{Bu})$	4	239.0	228.0 (O)	125.2	[167]
3 thf	$N(SiMe_2CH_2)_2$	5	233.6	240.2 (O)	136.8[b]	[153b]

a) Coordination number 4+2 due to two additional agostic interactions to trimethylsilyl groups;
b) trigonal bipyramidal environment of Ca with the amido ligands in equatorial positions.

The enhancement in reactivity which have been tendered by replacement of the donor ligand L (thp, thf) was also not sufficient to accomplish the hydroamination reactions. This work was published in 2013.[164]

3.1.2 Synthesis and characterization of the calciate complex $[K_2Ca\{N(H)Dipp\}_4]_\infty$ [**2**].

The fact that monometallic calcium-bis(amide) does not mediate the hydroamination reactions, raises the question of the cooperation of potassium and calcium in the catalyst system. *MULVEY* and his coworkers, reported that mixed alkali-metal-magnesium alkylamides tend to form inverse crowns which react as highly reactive metalation reagents.[172] Hence, the work here focused on the enhancement of our calcium catalyst via the formation of heterobimetallic s-block metal amides $[K_2Ca\{N(H)Dipp\}_4]_\infty$ which can only be prepared in presence of excess potassium amide KNHDipp, while the stoichiometric reactions led to homometallic complexes such as b, c, d, e, f, g, and h complexes as shown in **Scheme 3.2**.



Scheme 3.2: Synthesis of heterobimetallic $[K_2Ca\{N(H)Dipp\}_4]_\infty$ [**2**].

The calciate complex [**2**] has been precipitated from a THF solution as a solvent-free coordination polymer. Mixed metal amide complexes often behave differently than the homometallic congeners. However, a comparison on the basis of NMR parameters of b, c, d, e, f, g and [**2**] showed us similarities between these complexes with respect to the chemical shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra. These similarities can be explained by the dissociation of these complexes and dynamic behavior that is fast on the NMR time scale. These parameters verify that complex [**2**] breaks up its polymeric structure in the solution, which also explains the good solubility in common organic donor solvents. A section of the

polymeric solid state structure of [**2**] including the heterobimetallic amide with a ratio of 2:1 for K:Ca is shown in **Figure 3.2**. It is obvious that the less electropositive metal Ca binds to the amido-ligand, forming a calciate, while the more electropositive metal K represents the counter cation.

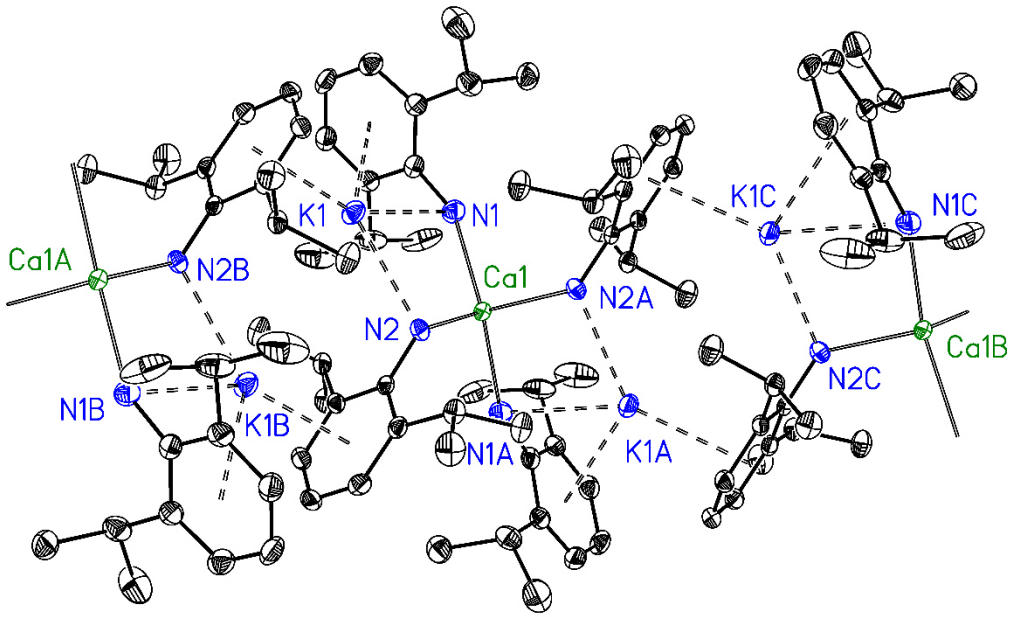


Figure 3.2: Section of the polymeric solid state structure of [**2**]. The ellipsoids represent a probability of 40 %, H atoms are neglected for clarity. The letters A (-x, y, -z + 0.5) and B (-x, -y + 2, -z) characterize symmetry-related atoms. Selected bond lengths (pm): Ca1-N1 232.9(3), Ca1-N2 239.3(3), K1-N1 294.1(3), K1-C1 292.9(3), K1-N2 287.2(3), K1-C13B 335.0(3), K1-C14B 324.1(3), K1-C15B 308.8(3), K1-C16B 304.2(4), K1-C17B 312.1(3), K1-C18B 327.4(3), N1-1 137.9(4), N2-C13 137.9(4). Selected bond angles (deg): N1-Ca1-N2 100.3(1), N1-Ca1-N1A 152.4(2), N1-Ca1-N2A 98.6(1), N2-Ca1-N2A 93.2(1), Ca1-N1-C1 = 155.8(3), Ca1-N1-K1 90.5(1), Ca1-N2-C13 127.0(2), Ca1-N2-K1 90.93(9).

The calcium atom is in a distorted tetrahedral environment with N-Ca-N angles between 93.2(1) and 153.4(2)°. Despite the small coordination number of 4, rather large Ca-N bond lengths of 232.9(3) and 239.3(3) pm are observed due to electrostatic repulsion between the amide anions and intramolecular steric strain between the bulky aryl groups of neighboring amido ligands. The flexibility of the Ca-N-C bond angles (155.8(3) and 127.0(2)°) supports the mainly ionic nature of this compound. These tetrakis(anilido)calciates are interconnected

by potassium counter cations that bind to the nitrogen atoms (K-N = 287.2(3) and 294.1(3) pm) and saturate their coordination spheres by Lewis acid-base interactions to the π-systems of the aryl groups. The high reactivity and the efficiency of this complex to catalyze hydrofunctionalization reaction (hydropentelation such as: hydroamination and hydrophosphanylation) will be shown in a later chapter, can be understood based on: firstly, the pK_a values of arylamines (approx. 31 depending on the substitution pattern) are higher than the pk_a values of most common primary amines such as aniline (30.6), secondary amines like *N*-methyl-aniline (29.5), diphenylamine (25.0) and than the pK_a value of diphenylphosphane (22.9), which enables the deprotonation of these substrates.[173] Secondly, in comparison with complex [**1**], the small coordination number of calcium and the varying N-Ca-N angles between 93.2(1)° and 153.4(2)° enhance the reactivity in comparison to the calcium complex [**1**] with angles of around 120°. Due to these findings, the calcium atom is less shielded and the accessibility of calcium by the substrate in complex [**2**] is facilitated. Furthermore, complex [**2**] has a remarkable enhancement of the nucleophilicity of the anilide anions, caused by the electrostatic repulsion between the anilide anions and the electron-donating isopropyl groups. Overall complex [**2**] is a solvent-depleted complex, whereas solvent-free calcium amides like complex [**1**] dimerize via bridging amido ligands.[168] Additionally, the potassium ions form strong bonds to the aromatic π-systems of the aryl groups, preferring a side-on coordination to the phenyl groups.[174] HASB theory supports the notion that the potassium ion represents a significantly softer cation (Lewis base) than the lighter alkaline metals ions and the doubly charged calcium ions. In heterobimetallic amides of potassium and calcium, the amido anions always bind to the harder and less electropositive divalent calcium ion, forming tetrakis(amido)calciates with tetra-coordinate calcium centers. This work was published in April 2013.[162b]

3.2 Reactivity of $[K_2Ca\{N(H)Dipp\}_4]_\infty$ [**2**] in hydropentelation (N, P) reactions.

In calcium-mediated catalytic processes, the calciate $[K_2Ca\{N(H)Dipp\}_4]$ (Dipp = C_6H_3-2,6-*i*-Pr_2) [**2**] represents an ideal choice because its preparation is straightforward from the metathesis reaction of K{N(H)Dipp} with CaI_2, its purification easily succeeds by recrystallization, this complex crystallizes without ligated ether bases and consequently, it can be weighed, handled and stored under an inert atmosphere without aging of the crystalline material due to desolvation and loss of ethereal coligands. In addition, smaller amines easily replace the bulky Dipp-NH_2 via transamination reactions in order to release steric pressure.[162b] For evaluation purposes, we maintained both, the diyne system diphenylbutadiyne (due to commercial availability and low costs) and the used catalyst [**2**] under variation of the reaction conditions and substitution pattern of the primary and secondary arylamines as well as phosphanes.

3.2.1 Addition of primary arylamines

At the beginning of this work, the reactivity of complex [**2**] has been studied by using this complex to mediate the addition of several primary arylamines (**Figure 3.3**) across the chosen diyne system.

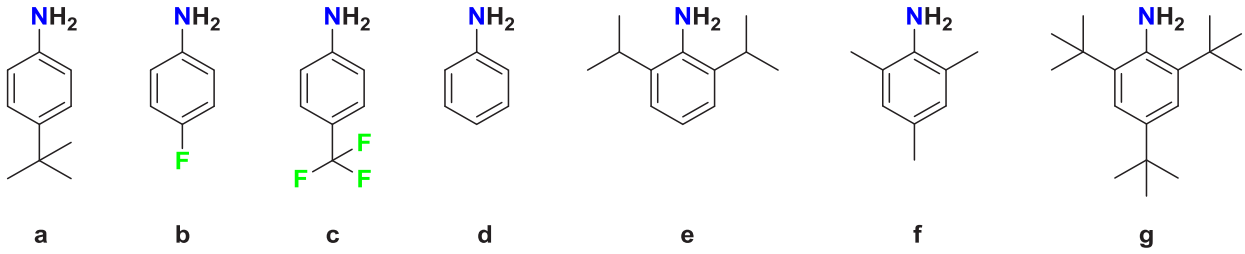
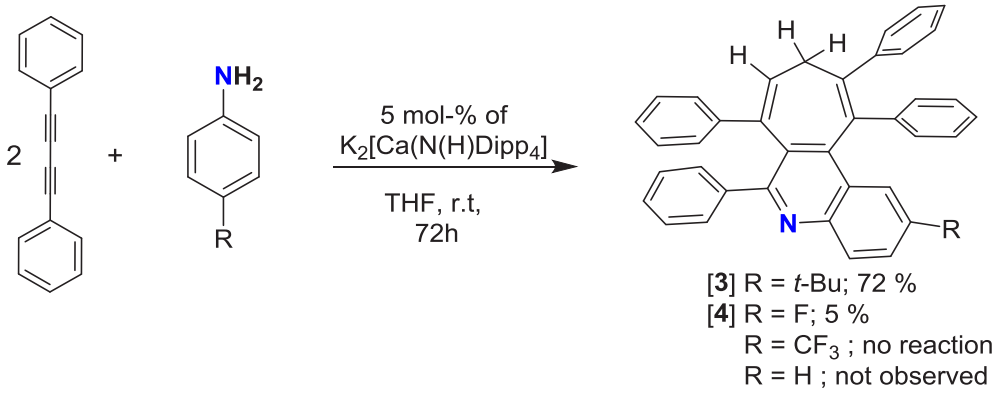


Figure 3.3: The investigated primary arylamines.

Equimolar amounts of diphenylbutadiyne and substituted primary amines were combined in THF in the presence of 5 mol-% of complex [**2**] and stirred for three days at room temperature. Afterwards a hydrolytic work-up procedure, an unusual product has been formed, similar to the observation of formation of the naphthalene side product which has

been reported by *GLOCK* et al.[162c] The reaction of one equivalent of 4-*tert*-butylaniline with two equivalents of diphenylbutadiyne under the above mentioned conditions give product [**3**] with a yield of 72 % as shown in **Scheme 3.3**.



Scheme 3.3: The reaction of differently substituted anilines (**a**, **b**, **c, d)** with diphenylbutadiyne, in THF at room temperature.

The formation of product [**3**] is based on α-deprotonation steps of 4-*tert*-butylaniline and formation of a C-C bond leading to 2-*tert*-butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline.

The ^{1}H NMR spectrum of [**3**] clearly shows a characteristic ABX coupling pattern for the hydrogen atoms at the seven-membered ring leading to three doublets of doublets (**Figure 3.4**) with a pseudo-triplet for the CH resonance at δ = 6.41 ppm due to very similar vicinal coupling constants. The H atoms of the methylene fragment are magnetically inequivalent with a geminal coupling constant of $^{2}J_{H,H}$ = 11.6 Hz and verifying the non-planarity of the cycloheptatriene unit.

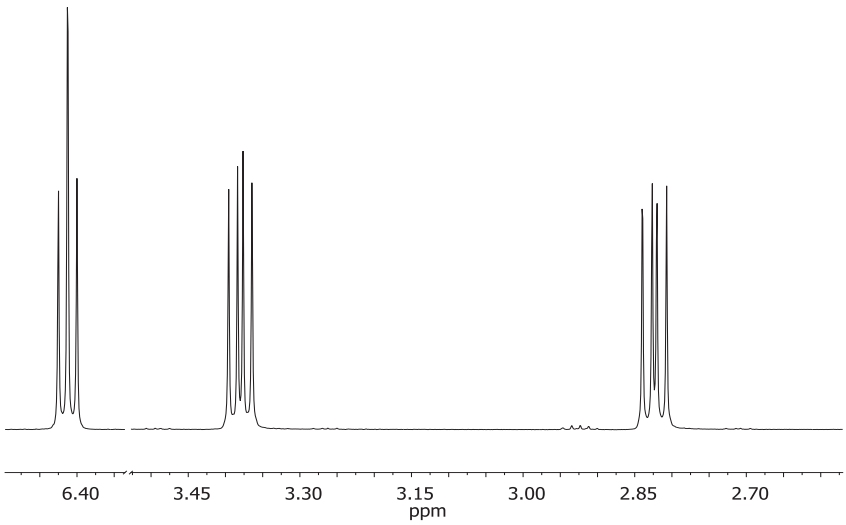


Figure 3.4: ^{1}H NMR resonances (400.08 MHz, [D_8]THF, r.t) of the hydrogen atoms of the seven-membered ring of compound [**3**].

In order to propose a reaction mechanism, we repeated the preparation of this compound with partly *N*-deuterated 4-*tert*-butylaniline with a deuteration degree of 75 %. This approach yields compound [**3**], besides its partly deuterated derivatives. The coupling pattern in the ^{1}H NMR spectrum at the CH signal at δ = 6.41 ppm enables the assignment and determination of the positions of deuterium atoms (**Figure 3.5**). The coupling pattern of the endocyclic =CH-CH_2- fragment allows the assignment to the moieties CH-CH_2, CH-CHD, and CH-CDH. The intensity ratio of the resonances excludes the formation of CH-CD_2 units, which would suggest a bimolecular reaction mechanism. This coupling pattern and the resonances of the neighboring methylene group clearly show that there exists no preference for the deuteration at either position and hence no stereo control for the transfer of the *ortho*-hydrogen atom of the 4-*tert*-butylphenyl group to the seven-membered ring yielding the methylene group C2B.

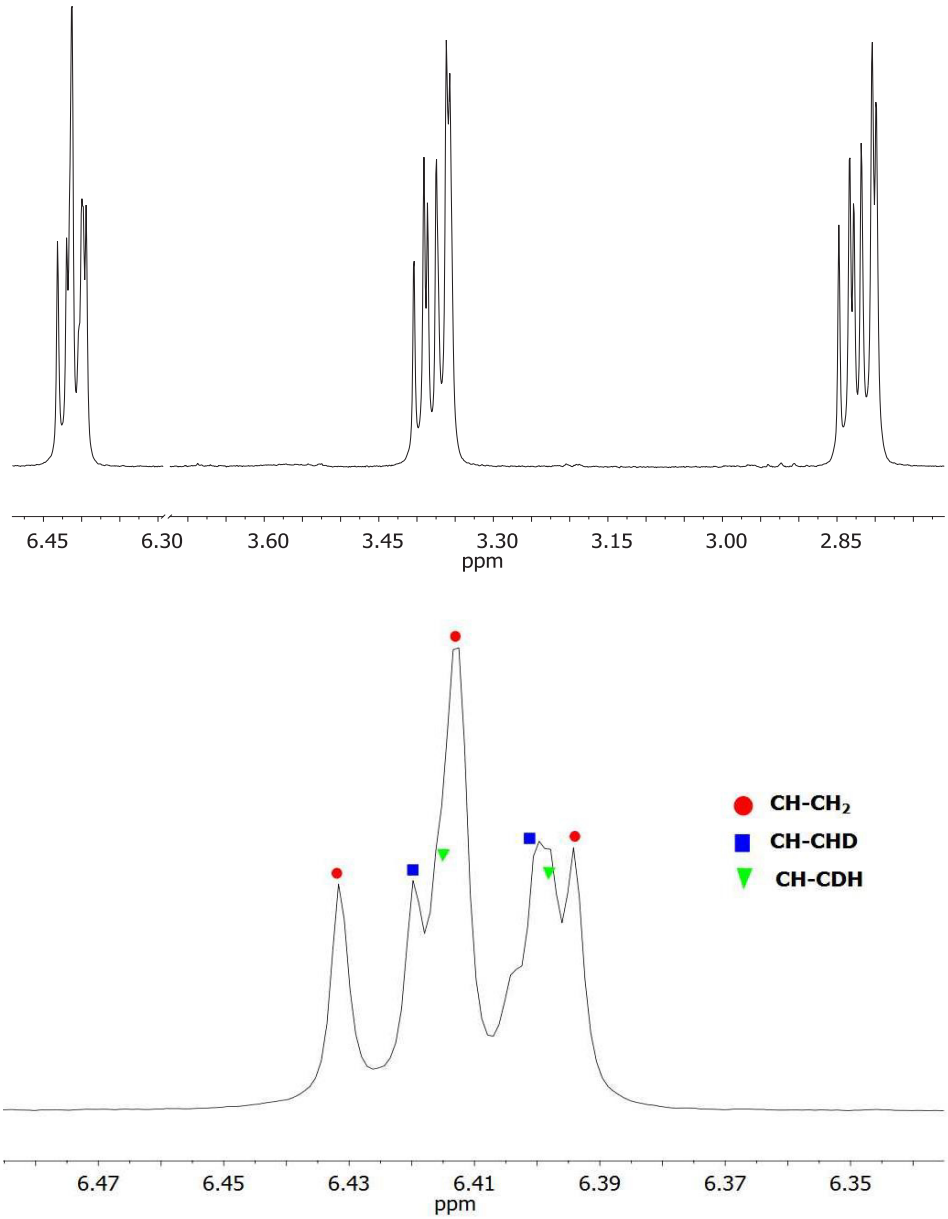


Figure 3.5: ^{1}H NMR spectrum of the C-H fragments of the seven-membered ring of partly deuterated [**3**] (top) and with assignment to differently deuterated derivatives (bottom), for the CH group at δ = 6.41 ppm.

In order to determine the influence of the *tert*-butyl in the used arylamine (**Figure 3.3, a**), we investigated several *para*-substituted arylamines (**Figure 3.3**, **b**, **c**, **d**). Alteration of the electronic and steric nature of the *para*-substituent from a electron donating group (*tert*-butyl (**Figure 3.3, a**)) to an electron withdrawing group (fluoride (**Figure 3.3, b**) gave similar products as shown in **Scheme 3.3**, [**4**]).

2-Fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinolne (product [**4**]) was obtained in very low yield because the fluoro substituent withdraws electron density through the conjugated π-system of the aromatic ring from the nitrogen atom, reducing the nucleophilicity of the amino functional moiety.[175] Verification of the compositions of [**3**] and [**4**] succeeded also by X-ray diffraction experiments at single crystals. Molecular structures and numbering schemes of [**3**] and [**4**] are presented in **Figure 3.6** ([**3**] is top and [**4**] is bottom). The numbering scheme of both compounds is similar and a comparison of selected bond lengths is given in **Table 3**. These compounds are built from two butadiyne molecules (atoms C1A to C16A and C1B to C16B) and one 4-*tert*-butylaniline (N1A, C17A to C26A) or 4-fluoroaniline (N1A, F1A, C17A to C22A), respectively. The quinoline fragments show balanced bond lengths which are comparable to those of unsubstituted quinoline.[176] Substituents at the quinoline nucleus of [**3**] and [**4**] lead to a slight lengthening between those carbon atoms carrying substituents. The phenyl groups are oriented nearly perpendicular to the ring systems and hence, no interaction between the aromatic phenyl groups and the π-systems of the seven-membered ring can be expected and characteristic C-C single bond values around 149 pm were observed.

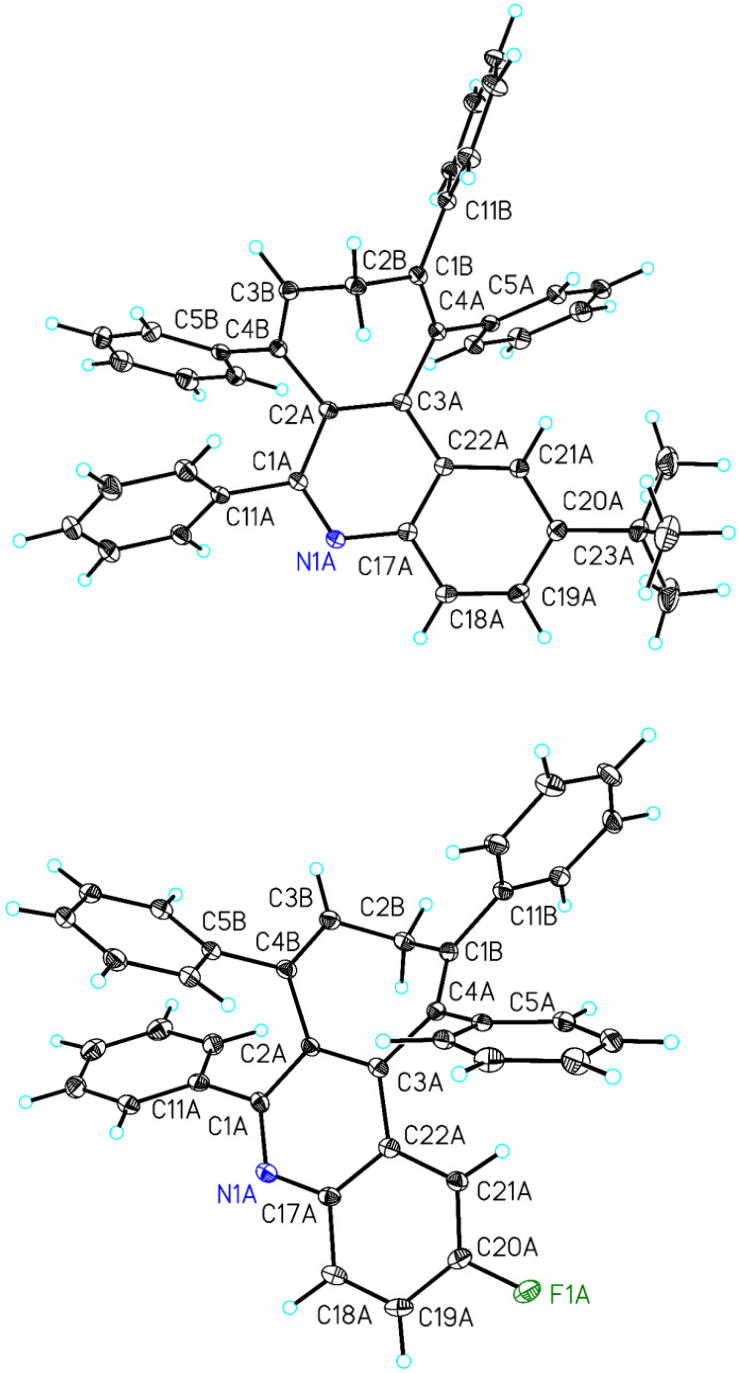


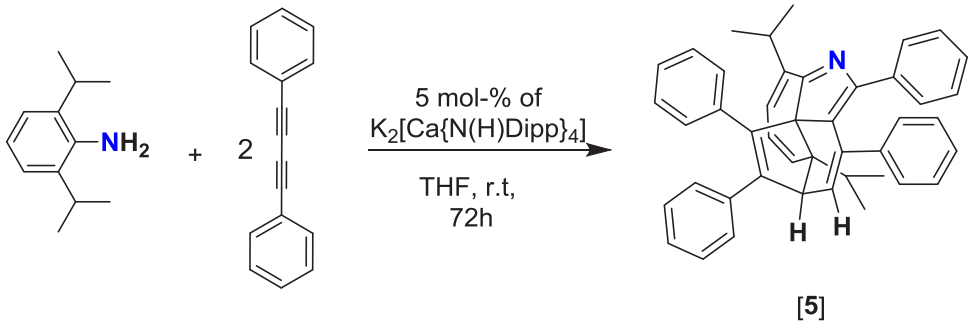
Figure 3.6: Molecular structures and numbering schemes of [3] (top) and [4] (bottom). The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths are given in **Table 3**.

Table 3: Comparison of selected bond lengths (pm) of 2-(*tert*-butyl)-6,7,10,11-tetraphenyl-9*H*-cyclohepta[c]quinoline [**3**] and 2-(fluoro)-6,7,10,11-tetraphenyl-9*H*-cyclohepta[c]quinoline [**4**].

Bond	[**3**] (R = *t*-Bu)	[**4**] (R = F)
N1A-C1A	131.4(2)	131.4(3)
N1A-C17A	137.1(2)	138.0(3)
C17A-C18A	140.8(2)	141.5(3)
C17A-C22A	141.6(2)	141.5(3)
C18A-C19A	137.0(2)	137.5(4)
C19A-C20A	141.4(2)	138.7(4)
C20A-C21A	138.5(2)	136.4(3)
C20A-R	153.2(2)	136.3(3)
C21A-C22A	141.6(2)	141.9(3)
C1A-C2A	144.4(2)	144.2(3)
C1A-C11A	149.1(2)	149.6(3)
C2A-C3A	139.5(2)	139.5(3)
C2A-C4B	148.6(2)	148.3(3)
C3A-C4A	149.2(2)	148.6(3)
C3A-C22A	144.6(2)	146.2(3)
C4A-C5A	149.4(2)	149.4(3)
C4A-C1B	135.6(2)	135.8(3)
C1B-C2B	151.8(2)	151.1(3)
C1B-C11B	149.0(2)	149.3(3)
C2B-C3B	150.3(2)	150.5(3)
C3B-C4B	133.8(2)	132.8(3)
C4B-C5B	149.0(2)	149.2(3)

To ensure our finding we used similar arylamines with a strongly electron withdrawing group (Trifluoromethyl **Figure 3.3**, **c**). But due to the fact that trifluoromethyl group is a stronger electron withdrawing group and bulkier than the fluoro group,[175] no reaction was observed even after applying of harder reaction conditions (refluxing, longer reaction time or higher load of the catalyst). Using unsubstituted arylamine (aniline, **Figure 3.3**, **d**) under the previously applied reaction conditions (5 mol-% of the catalyst and 3 days stirring at room temperature) did also not lead to the formation of a similar product. This finding led us to conclude that the used primary arylamine should be substituted with an electron

donating group such as methyl, isopropyl or *tert*-butyl. Therefore, the arylamines **e**, **f** and **g** (**Figure 3.3**, **e**, **f**, **g)** were investigated. The common features of these three arylamines are that the ortho substitutes are blocked by alkyl groups (methyl, isopropyl or *tert*-butyl). Consequently, the reaction with diphenylbutadiyne must proceed via a different pathway without *ortho*-CH activation. The reaction of 2,6-diisopropylaniline with diphenylbutadiyne in a 1:2 ratio for 3 days at room temperature in THF in the presence of a precatalyst load of 5 mol % of $K_2[Ca\{N(H)Dipp\}_4]$ according to **Scheme 3.4** gives the tetracyclic imine 2,6-diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.0^{1,7}.0^{2,13}]pentadeca-3,5,7,9,11,14-hexaene [**5**] with a yield of 82-%.



Scheme 3.4: Calciate-mediated hydroamination of diphenylbutadiyne with 2,6-diisopropylaniline in tetrahydrofuran yielding tetracyclic imine [**5**].

Verification of the composition of [**5**] succeeded also by X-ray diffraction experiments of single crystals. Molecular structure and numbering scheme of [**5**] is presented in **Figure 3.7**. The labeling of the atoms shows the numbering in accordance with the chemical name for the inner tetracyclic unit, with the nitrogen atom N8 being in position 8. For the numbering of the substituents, the digit of the adjacent ring atom was expanded by an additional digit to distinguish the carbon atoms within a substituent.

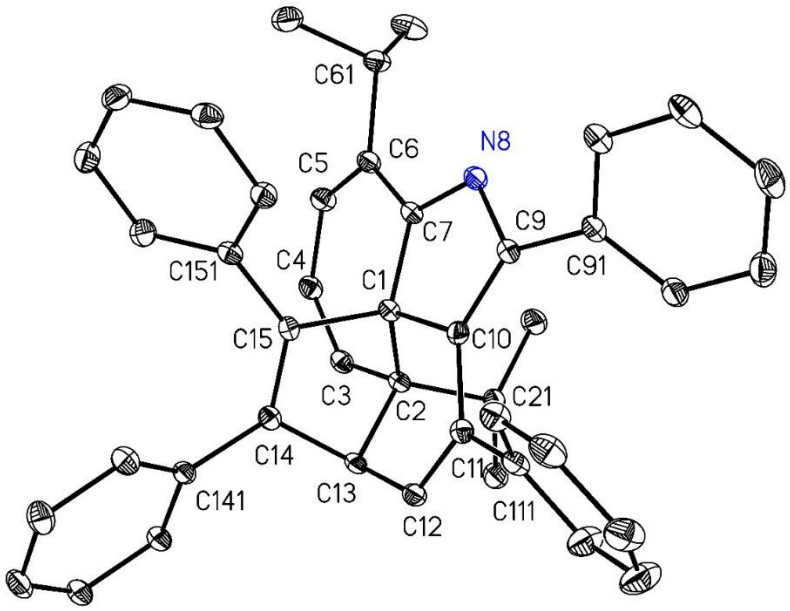
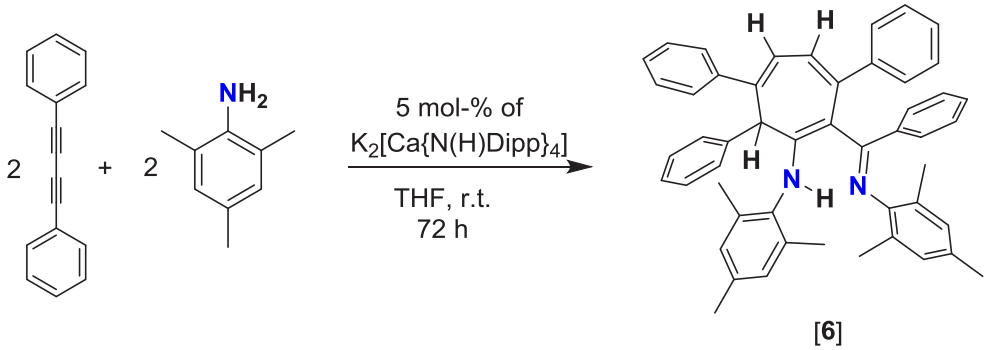


Figure 3.7: Molecular structure and numbering scheme of [**5**]. The ellipsoids represent a probability of 40 %, all H atoms are omitted for clarity reasons. Selected bond lengths (pm): C1-C2 156.2(2), C1-C7 150.2(2), C1-C10 151.6(2), C1-C15 154.8(2), C2-C3 150.4(3), C2-C21 155.2(3), C3-C4 134.1(3), C4-C5 145.7(3), C5-C6 135.2(3), C6-C7 144.4(3), C6-C61 152.4(3), C7-N8 131.2(2), N8-C9 141.8(2), C9-C10 136.6(3), C9-C91 147.9(3), C10-C11 145.0(2), C11-C12 135.5(3), C11-C111 149.0(3), C12-C13 151.1(3), C13-C14 153.3(3), C14-C15 134.2(3), C14-C141 147.5(2), C15-C151 147.7(3).

The nitrogen atom N8 is bound in a five-membered ring with a C7=N8 double bond and a N8-C9 single bond of 131.2(2) and 141.8(2) pm, respectively. Depending on these values, it is obvious that there is no significant delocalization within the conjugated system. A vast steric strain is introduced at the C1 atom, which is a member of all four cycles. This fact leads to severe deviations from a tetrahedral environment (C-C1-C values vary from 101.2(1) to 120.3(2)°) toward a trigonal- pyramidal environment (according to *HOUSER* and coworkers, the simple four-coordinate geometry index τ_4 allows determination of the geometry of tetra-coordinate atoms by applying the equation $\tau_4 = [360° - (\alpha + \beta)]/141°$, with α and β being the largest angles. Values of 1 and 0 for τ_4 are obtained for ideal tetrahedral and square-planar environments, respectively, whereas 0.85 and values between 0.07 and 0.64 are symptomatic of trigonal-pyramidal and seesaw geometries, respectively.[177] For C1 in compound [**5**] this concept gives a value of $\tau_4 = 0.88$). In addition, the C1-C bonds are

significantly elongated. The adjacent C2 atom shows even stronger deviations from the ideal tetrahedral geometry. The smallest C1-C2-C13 angle shows a value of only 95.7(1)° between three sp^3-hybridized carbon atoms and a C2-C13 bond length of 157.5(2) pm. Distortions also widen the angles at the vicinal diphenylethene fragment with C15-C14-C141 and C14-C15-C151 values of 129.9(2) and 130.1(2)°, respectively. In addition, compound [**5**] contains three chiral carbon atoms at positions C1, C2 and C13, consequently, 8 isomers (2^n), but due to the centric triclinic space group ($P\bar{1}$), the ring strain and the steric effects, the crystalline state consists only two of racemate of isomers.

Reaction of a less bulky amine, which is substituted at the *ortho*-positions by methyl groups, with the same diyne system led to different result. In this case, 2,4,6-trimethylaniline (**Figure 3.3**, **f**) and diphenylbutadiyne react at room temperature in THF with a 1:1 ratio in the presence of 5 mol-% of $K_2[Ca\{N(H)\text{-}Dipp\}_4]$ yielding *N*-mesityl-7-(*E*)-((mesitylimino)(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine [**6**]. As shown in **Scheme 3.5**, only those hydrogen atoms are depicted which were transferred from the nitrogen atom of the amine substrate to the carbon atoms of the seven-membered ring.



Scheme 3.5: Calciate-mediated hydroamination of diphenylbutadiyne with 2,4,6-trimethylaniline yielding *N*-mesityl-7-(*E*)-((mesitylimino)(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine [**6**].

Compound [**6**] represents an asymmetric *β*-diketimine derivative with an annelated unsaturated seven-membered ring. This structural fragment gives rise to a low field shifted resonance for the N-H···N hydrogen bridge in the ^{1}H NMR spectrum with a chemical shift of δ = 12.85 ppm. In **Figure 3.8**, the ^{1}H NMR spectrum of the methyl region is depicted.

This spectrum shows that the 2- and 6- positions are magnetically not equivalent which suggests a hindered rotation of the mesityl groups around the N-C bonds. The non-equivalence of the *ortho*-methyl groups of each mesityl substituent is also a consequence of the chiral carbon atom of the seven-membered cycloheptatriene ring.

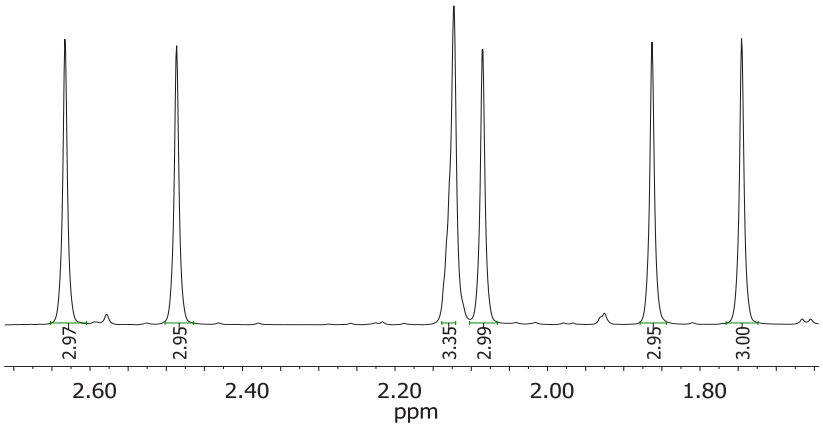


Figure 3.8: The ^{1}H NMR resonances of the methyl substituents of the mesityl groups.

Molecular structure and numbering scheme of compound [**6**] are shown in **Figure 3.9**. This compound is built from two butadiyne (atoms C1A to C4A and C1B to C4B) and two 2,4,6-trimethylaniline molecules (N1A, C17A to C25A as well as N1B, C17B to C25B). Compound [**6**] contains the chiral C4B atom but due to the centric monoclinic space group, the crystalline state consists of a racemate of R- and S-isomers. The structure dominating moiety is the N1A-C1B-C2B-C3B-N1B fragment with significant charge delocalization and a N1B-H···N1A hydrogen bridge (N1A···N1B distance: 265.7(3) pm). The C1A-C2B bond length shows a characteristic single bond value for sp^2 hybridized carbon atoms, excluding π-interaction between the *β*-diketimine unit and the remaining π-bonds of the seven-membered ring. The hydrogen bridge also explains why only the (*E*)-isomer of the N1A=C1B imine unit is observed.

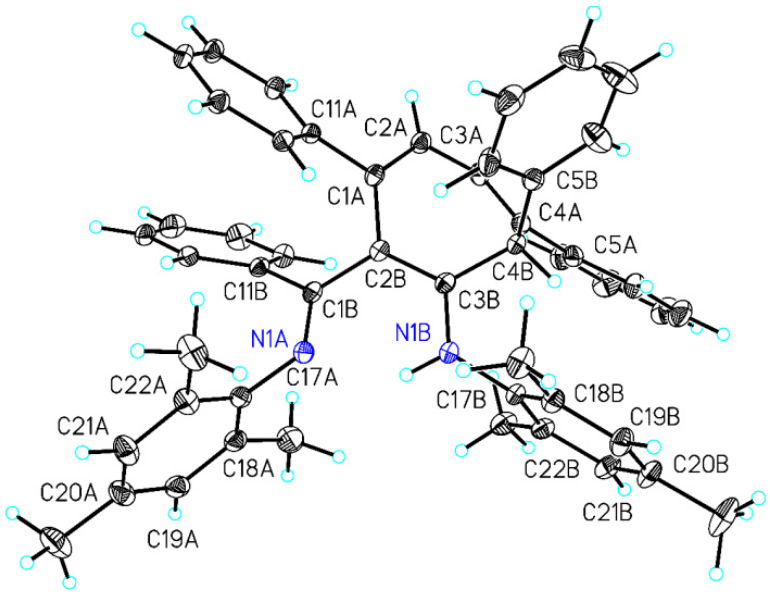
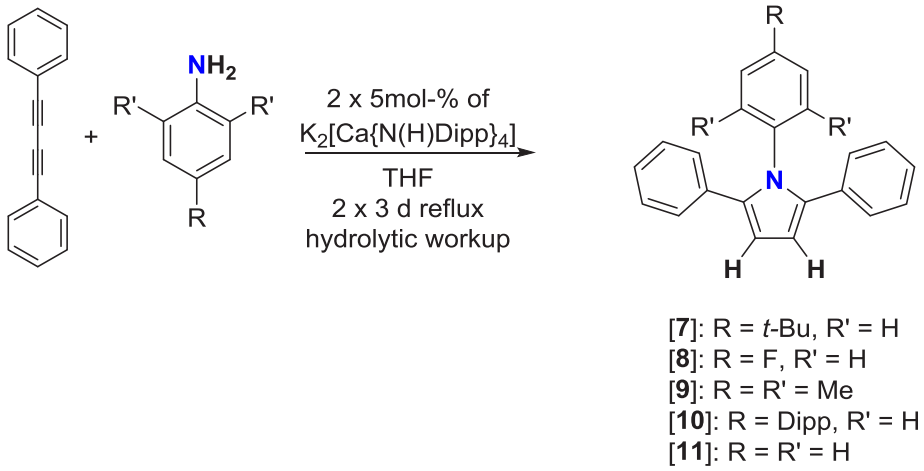


Figure 3.9: Molecular structure and numbering scheme of [**6**]. The ellipsoids represent a probability of 30 %, selected H atoms are shown with arbitrary radii. Selected bond lengths (pm): N1A-C17A 142.9(3), N1A-C1B 129.5(3), N1B-C17B 143.2(3), N1B-C3B 135.7(3), N1B-H 88(3), C1A-C2A 135.8(3), C1A-C2B 147.2(3), C1A-C11A 149.0(3), C2A-C3A 143.9(3), C3A-C4A 134.7(3), C4A-C5A 148.4(3), C4A-C4B 152.8(3), C1B-C2B 146.9(3), C1B-C11B 150.6(3), C2B-C3B 139.1(3), C3B-C4B 151.6(3), C4B-C5B 153.9(3).

In contrast, no reactions were observed between 2,4,6-tri-*tert*-butylaniline (**Figure 3.3**, **g**) and diphenylbutadiyne under the same reaction conditions (5 mol-% of catalyst and 3 days stirring at room temperature), even though this arylamine is substituted with three electron donating groups (*tert*-butyl) which could be expected to increase the nucleophilicity by increasing the electron density through the conjugated π-system of the aromatic ring at the nitrogen atom. The inactivity of arylamine **g** even while applying harsher reaction conditions, such as refluxing, higher catalyst load or longer time (stirring up to six days), can be referred to the huge steric effect which is caused by the substitution in *ortho*- and *para*-positions by *tert*-butyl. Consequently, arylamine **g** cannot easily replace the bulky Dipp-NH_2 in the catalyst via transamination reactions in order to release steric pressure. Mechanistically, the aryl Mes* hinders the attack at butadiyne.

In order to study the influence of the reaction temperature, we repeated the previous reactions between the primary arylamines (**Figure 3.3**) and the diphenylbutadiyne under harsher conditions. The addition of the arylamines (**a**, **b**, **d**, **e** and **f**) to diphenylbutadiyne was performed in THF in the presence of 5 mol -% of the catalyst [**2**] with stirring and refluxing

of the reaction mixture for three days. Then additional 5 mol-% of $K_2[Ca\{N(H)Dipp\}_4]$ [**2**] were added and heating was continued for further three days. A standard workup procedure, including hydrolysis with distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from pentane or toluene at 5 °C yielded colorless crystals of *N*-aryl-2,5-diphenyl-pyrroles according to **Scheme 3.6** ([**7**]: R = *t*-Bu, R' = H; [**8**]: R = F, R' = H; [**9**]: R = R' = Me; [**10**]: R = Dipp, R' = H; [**11**]: R = R' = H). In contrast, application of these new harsh reaction conditions for the arylamines **c** (4-trifluoromethylaniline) and **g** did not lead to any increase of their reactivity and no reactions were observed.



Scheme 3.6: Complex [**2**] mediated hydroamination of diphenylbutadiyne with primary arylamines at high temperatures yielding *N*-Aryl-2,5-diphenyl-pyrroles.

Only those hydrogen atoms that were bound at the nitrogen atom of the amine substrate are depicted. Due to the symmetry of these compounds [**7**-**11**], the ^{1}H NMR spectra show singlets for the C*H* resonances around δ = 6.41 ppm. The X-ray diffraction experiments on single crystals succeeded only for compounds [**9**] and [**11**]. The molecular structure and numbering scheme of *N*-mesityl-2,5-diphenylpyrrole [**9**] and *N*-phenyl-2,5-diphenylpyrrole [**11**] are depicted in **Figure 3.10** and **Figure 3.11**, respectively. Due to steric reasons, the N-bound aryl group is oriented nearly perpendicular to the pyrrole ring with an angle of 69.2° between these planes. Expectedly, the π-system of the pyrrole ring leads to short bonds and charge delocalization to a large extend. Endocyclic C1-C2, C2-C3 and C3-C4 bond lengths differ by less than 3 pm and have an average value of 138.9 pm. The exocyclic C1-C20 and

C4-C5 bond lengths with an average distance of 147.2 pm are characteristic for single bonds between sp^2-hybridized carbon atoms.

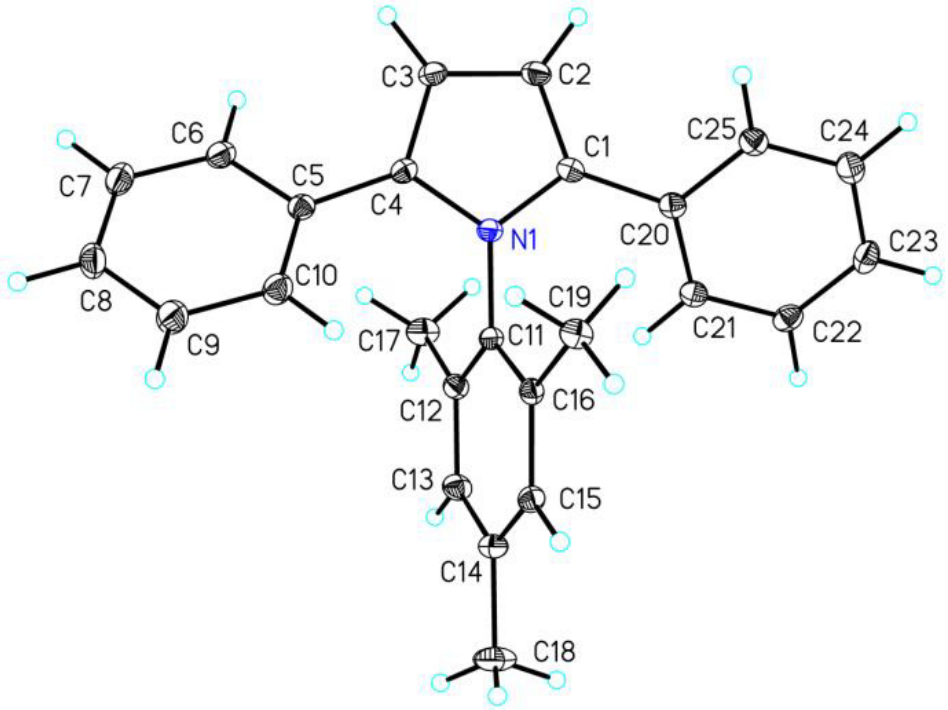


Figure 3.10: Molecular structure and numbering scheme of [**9**]. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (pm): N1-C1 139.1(2), N1-C4 139.3(2), N1-C11 144.4(2), C1-C2 138.1(2), C2-C3 140.7(2), C3-C4 137.8(2), C1-C20 147.6(2), C4-C5 146.8(2); angles (deg.): C1-N1-C4 109.0(1), N1-C1-C2 107.5(1), C1-C2-C3 107.9(1), C2-C3-C4 108.4(1), N1-C4-C3 107.3(1), C1-N1-C11 125.6(1), C4-N1-C11 125.1(1), N1-C1-C20 124.7(1), C2-C1-C20 127.8(1), N1-C4-C5 125.3(1), C3-C4-C5 127.4(1).

1,2,5-Triphenylpyrrole [**11**] exhibits crystallographic C_2 symmetry and shows very similar structural parameters in comparison to compound [**9**], as shown in **Figure 3.11**.

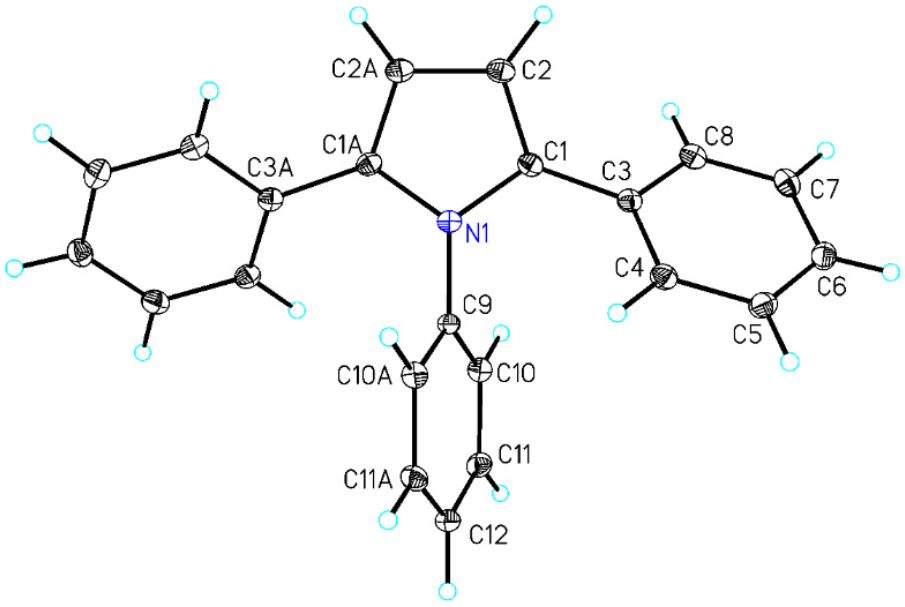
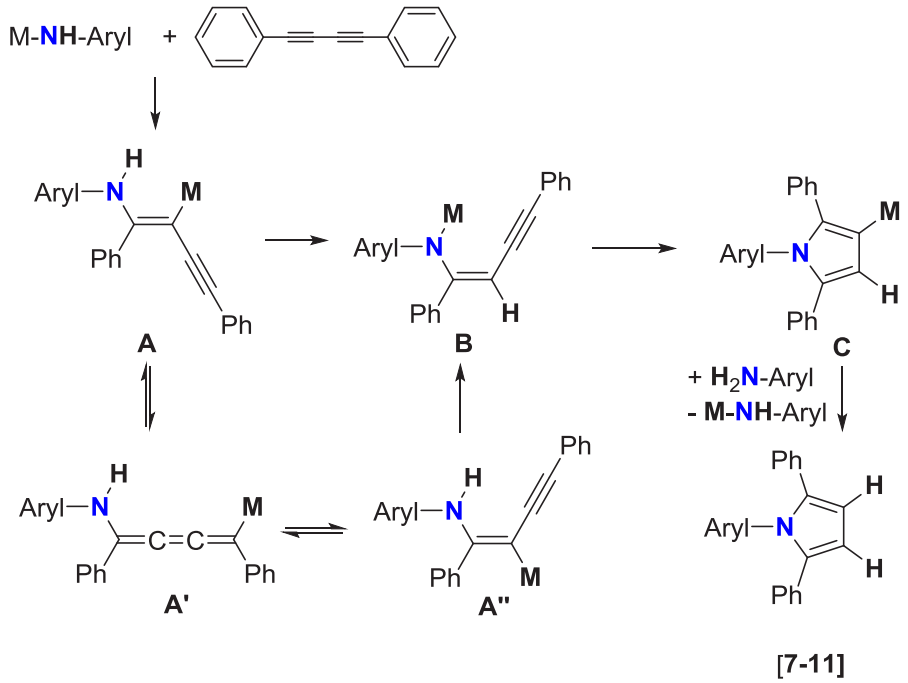


Figure 3.11: Molecular structure and numbering scheme of 1,2,5-triphenylpyrrole [**11**]. The ellipsoids represent a probability of 30 %, hydrogen atoms are shown with arbitrary radii. Symmetry-related atoms (-x+2, y, -z+1) are marked with the letter A. Selected bond lengths (pm): N1-C1 138.49(13), C1-C2 138.01(15), C2-C2A 141.7(2), and N1-C9 143.82(18).

Proposed mechanism

In all cases, with exception of [**3**], moderate to good yields were obtained. The precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ [**2**] reacts with the primary arylamines, and NMR spectroscopic investigations of THF solutions containing $K_2[Ca\{N(H)\text{-}Dipp\}_4]$ and the 4-fold stoichiometric amount of 2,4,6-trimethylaniline verified the quantitative ligand exchange and formation of 2,6-diisopropylaniline. A 1:2 ratio of [**2**] and mesitylamine led to heteroleptic calciates of the general formula $K_2[Ca\{N(H)Dipp\}_{4-x}\{N(H)\text{-}Mes\}_x]$. Due to the fact that all aniline derivatives might exhibit comparable pK_a values, it can be concluded that the bulkier amide is replaced by the smaller amide in order to minimize intramolecular strain of the calciate anion, mainly provoked by the ortho substituents. The catalytic reaction starts with the addition of a metal-nitrogen bond to one C≡C triple bond as shown in **Scheme 3.7**

(nucleophilic attack of an amide at an alkyne) yielding intermediate **A**. In this scheme, **M** symbolizes the s-block metal and hence the anionic site.

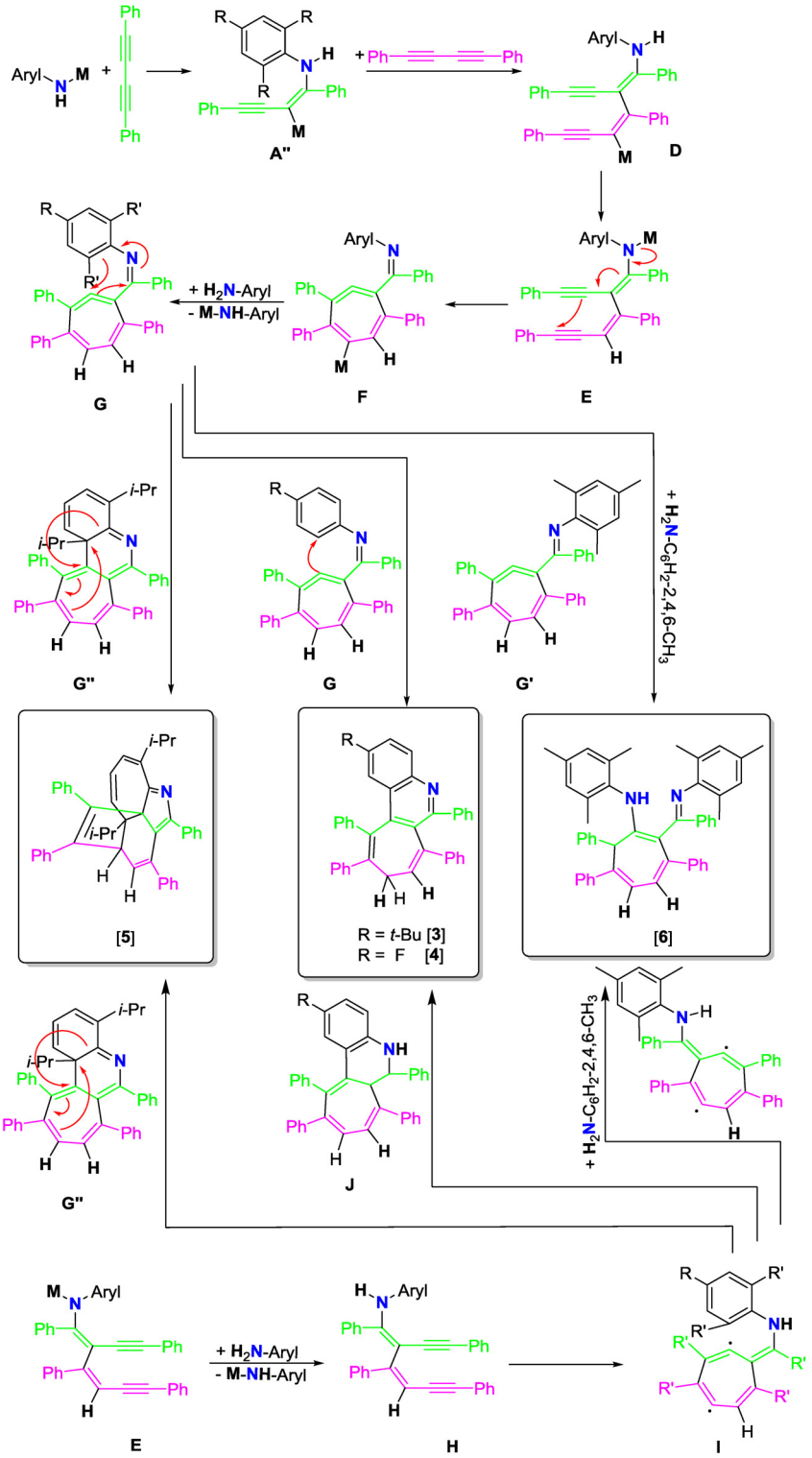


Scheme 3.7: Proposed mechanism of the complex [**2**] mediated hydroamination of diphenylbutadiyne with primary arylamines at high temperatures yielding *N*-aryl-2,5-diphenyl-pyrroles.

E/Z-Isomerization is possible via a cumulene isomer **A'** which can either isomerize to a *trans* (**A**) or a *cis* orientation (**A''**) of the anionic site and the remaining alkyne moiety. Such cumulene systems have also been suggested during calcium-mediated hydrophosphanylation of diphenylbutadiyne with diphenylphosphane in order to explain isomer mixtures.[51a] After the initial reaction step, intramolecular metalation transfers the *N*-bound hydrogen to the alkenyl moiety and amide **B** is formed. During the high temperature route an intramolecular addition to the second alkyne unit occurs and the pyrrole derivative **C** is formed. The reaction of this intermediate species with another arylamine regenerates the catalyst, and the formation of pyrroles [**7-11**] is completed. In contrast to this straightforward pathway for the synthesis of pyrroles [**7-11**], the low temperature route proceeds via an insertion of another diphenylbutadiyne molecule into the newly formed metal-carbon bond (carbometalation step, (**Scheme 3.8**)), yielding intermediate **D**. For the sake of clarity, the diphenylbutadiyne units are distinguished by different colors in this scheme. Thereafter an intramolecular

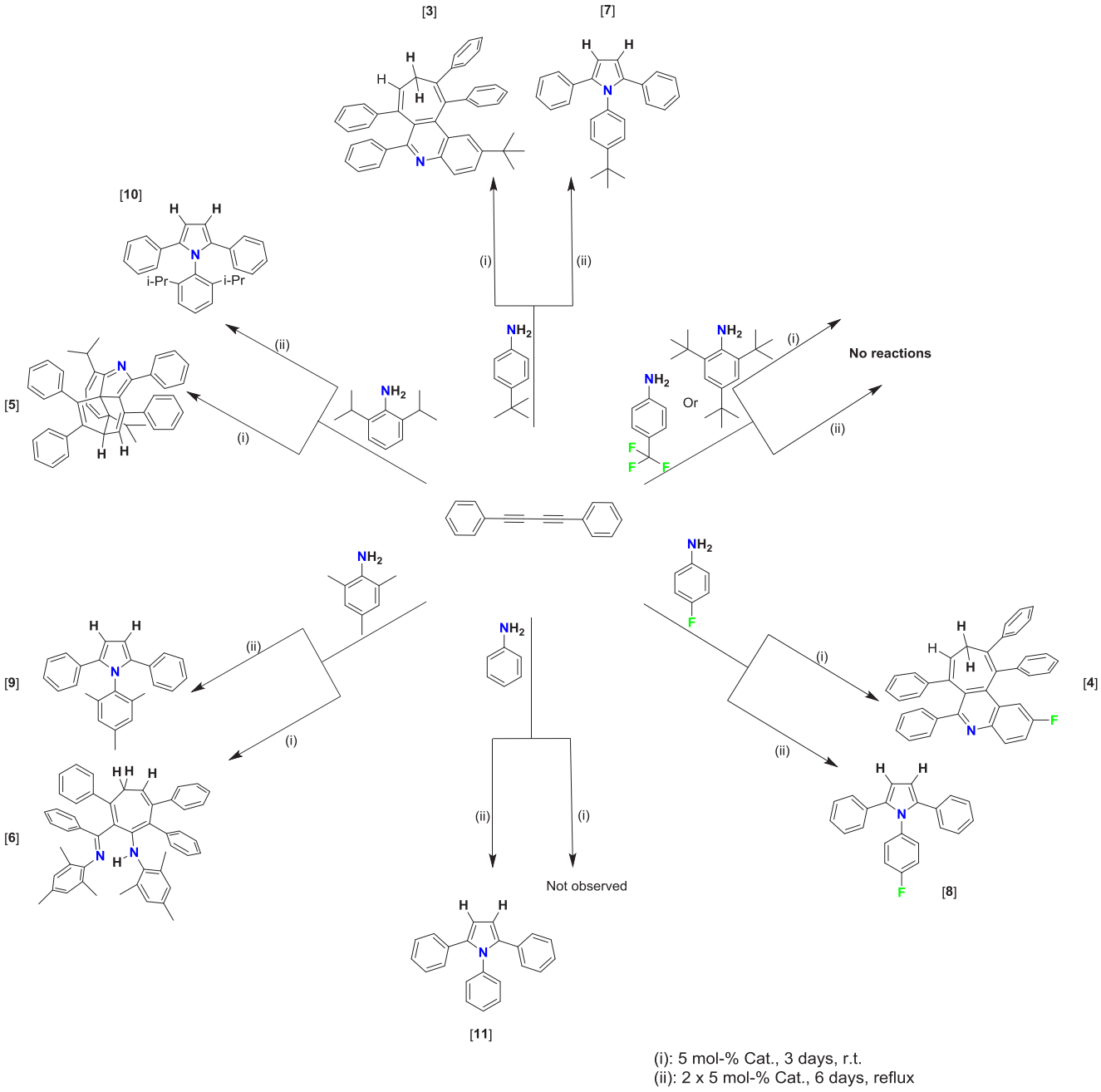
metalation forms amide **E** with a metal-nitrogen bond. Now, three reaction routes seem to be feasible to explain the formation of [**3**], [**4**] (via *ortho*-CH activation), [**5**] (via cyclization and rearrangement steps) and [**6**] (via addition of a second arylamine). The closed-shell ionic mechanism involves the formation of the 1,2,4,6-cycloheptatetraene intermediate **F** with the negative charge at the 5-position (exemplified in the scheme by an M-C bond). Such species exhibit ring strain, nevertheless, unsaturated ring systems of this kind have already been studied in a solid matrix[178] and by quantum chemical investigations, also considering other isomers such as phenylcarbene, bicyclo[3.2.0]hepta-1,3,6-triene, bicyclo[3.2.0]hepta-3,6-diene-2-ylidene, bicyclo[3.2.0]hepta-2,3,6-triene, and bicyclo[4.1.0]heptatriene.[179] Furthermore, a cyclotetramer of such a strained cycloheptatetraene derivative has been characterized by X-ray crystal structure determination.[180] These investigations show that 1,2,4,6-cycloheptatetraene is favored in comparison to a carbene set in a seven-membered ring, and represent 4n π-Möbius aromatic systems.[181] Afterward intramolecular metalation by an arylamine regenerates the catalyst and leads to the formation of **G**. In this bicyclic intermediate the allene moiety attacks the *ortho*-CH group leading to compounds [**3**] and [**4**]. Absence of *o*-CH fragments and bulkier N-bond aryl groups favor (in the case of methyl groups) the formation of isomer **G'**, leading to an alternative reaction pattern. Here, the 1,4-addtion of 2,4,6-Trimethylaniline to the cycloheptatetraene ring leads to the formation of compound [**6**]. In the case of Dipp groups, a cyclization reaction releases the strain of the seven membered ring which is caused by the allene moiety, and annihilates the aromatic character of the Dipp group, resulting intermediate **G''**, which rearranges and gives compound [**5**] as shown in **Scheme 3.8**. An alternative pathway which starts from the bottom of **Scheme 3.8**, allows the catalyst reformation by an intermolecular reaction with an arylamine and the protonation of **E** (hence, the formation of metal-free intermediate **H**). Thereafter, a *BERGMAN* cyclization leads to the formation of the diradical species **I**. This radical can attack either at an *o*-CH group giving intermediate **J**, which will yield [**3**] and [**4**] by the abstraction of the hydrogen from the amino functionality or in the case of preoccupation of *o*-positions of the arylamine by methyl group, another amine substrate will be added to intermediate **I**, leading to compound [**6**] as shown in **Scheme 3.8**. In the case of preoccupation of the *o*-positions of the arylamine by diisopropyl groups, the diradical species **I** will rearrange to the tricyclic imine **G''**, accompanied by a hydrogen abstraction from the

amino functionality. This hydrogen transfer from the amino unit to the carbon atom is accompanied by C-C bond formation, leading to a breakup of the aromaticity of the former Dipp group as shown in **Scheme 3.8**.



Scheme 3.8: Proposed mechanisms of the s-block metal-mediated hydroamination of diphenylbutadiyne with primary arylamines at room temperature via a 1,2,4,6-cycloheptatetraene intermediate (top) or a diradical species (bottom). The diphenylbutadiyne units are distinguished by the colors pink and green.

In summary, hydroamination of primary arylamines occurs successfully under two pathways depending on the reaction conditions (i): kinetic control (5 mol-% of the catalyst and 3 days stirring at room temperature) leads to rather complex reaction pathways, depending on the ortho-substituents of the arylamines and the formation of unsaturated seven-membered rings represents a key feature, or (ii) during thermodynamic control (2 × 5 mol-% of the catalyst and 2 × 3 days stirring and refluxing the hydroamination of diphenylbutadiyne with primary arylamines employing $K_2[Ca\{N(H)Dipp\}_4]$ yields *N*-aryl-2,5-diphenylpyrroles, as shown in the over-view scheme (**Scheme 3.9**) of the addition of primary arylamines (**Figure 3.3**) across diphenylbutadiyne.



Scheme 3.9: Addition of primary arylamines across diphenylbutadiyne under two different reaction conditions ((i) and (ii)).

This work was published in 2015.[182]

3.2.2 Addition of secondary arylamines

In order to shed light on the first reaction step we blocked one of the primary arylamine hydrogen atoms by using the *N*-methylatedanilines. *N*-methyl-aniline, *N*-methyl-*para*-tolylamine, *N*-methyl-4-fluoro-aniline and *N*-methyl-4-(trifluoromethyl)aniline (**Figure 3.12**, **h-k**).

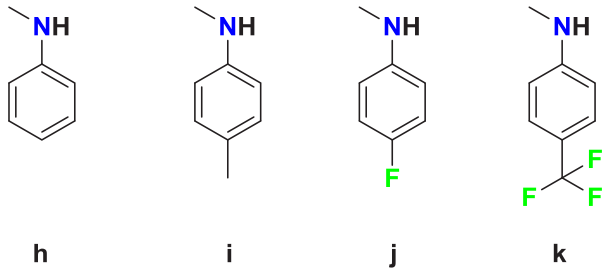


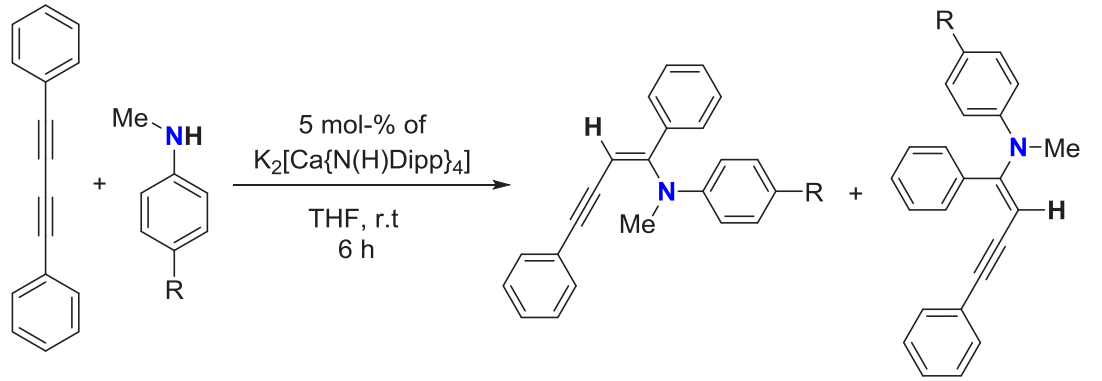
Figure 3.12: The investigated secondary arylamines.

GLOCK el at. showed that the hydroamination of diphenylbutadiyne with diphenylamine required a significantly reactive catalyst system such as dipotassium calciate [$K_2Ca(NPh_2)_4$]. During these calcium-mediated hydroamination reactions only singly hydroaminated butadiynes were isolated whereas the second C≡C triple bond remained intact.[162c] In contrast to theses initial investigations, the use of complex [**2**] to catalyze the hydroamination of diphenylbutadiyne with various secondary arylamines (**Figure 3.12**, **h-j**), gave surprising results, where the second C≡C triple bond of the butadiyne system was hydroaminated as well and doubly hydroaminated butadiynes were isolated.

Singly hydroaminated diphenylbutadiyne

In these studies, we used the same catalyst (complex [**2**]) as well as the same butadiyne system (diphenylbutadiyne) and diverse secondary arylamines. The use of secondary arylamines guarantees that the rather complex cyclization reactions are suppressed. *N*-Methyl-arylamines were reacted with diphenylbutadiyne in the presence of catalytic

amounts of $[K_2Ca\{N(H)Dipp\}_4]$([**2**]). In a standard procedure, diphenylbutadiyne was dissolved in THF. At room temperature, an equimolar amount of *N*-methyl-arylamine $HN(Me)C_6H_4$-4-R (R = H, Me, F, CF_3) and 5 mol-% of the catalyst were added. This solution was stirred for several hours at room temperature. Repeated NMR measurements showed that in all cases, with the exception of arylamine **k** (**Figure 3.12**, **k**), the conversion of the secondary arylamine and the formation of singly hydroaminated diphenylbutadiyne was successful (R = H [**12**], Me [**13**], F [**14**]) and mixtures of *E*- and *Z*-isomers according to **Scheme 3.10**. After quantitative conversion the reaction mixture was hydrolyzed with distilled water, the aqueous solution was extracted with diethyl ether. The ether fractions were combined, dried with sodium sulfate, then the ether was removed yielding the tertiary amines 1-(*N*-methyl-anilino)-1,4-diphenylbut-1-ene-3-yne with *E*/*Z* ratios of approximately 1 : 0.6 [**12**], 1 : 1 [**13**] and 1 : 0.9 [**14**].



	yield	isomer ratios	
R = H	[**12**], 92 %	*Z*-[**12**] 39 %	*E*-[**12**] 61 %
Me	[**13**], 88 %	*Z*-[**13**] 49 %	*E*-[**13**] 51 %
F	[**14**], 78 %	*Z*-[**14**] 48 %	*E*-[**14**] 52 %
CF_3	no reaction		

Scheme 3.10: Single hydroaminated diphenylbutadiyne.

Recrystallization from a solvent mixture of dichloromethane and pentane gave pure compounds. However, the different isomers exhibited rather similar solubility properties hampering a fractional crystallization under these conditions. Verification of the composition of [**12**], [**13**] and [**14**] was successful by X-ray diffraction experiments on single crystals. Molecular structures and numbering schemes of compounds [**12**], [**13**] and [**14**] are presented in **Figure 3.13**, **Figure 3.14** and **Figure 3.15**, respectively.

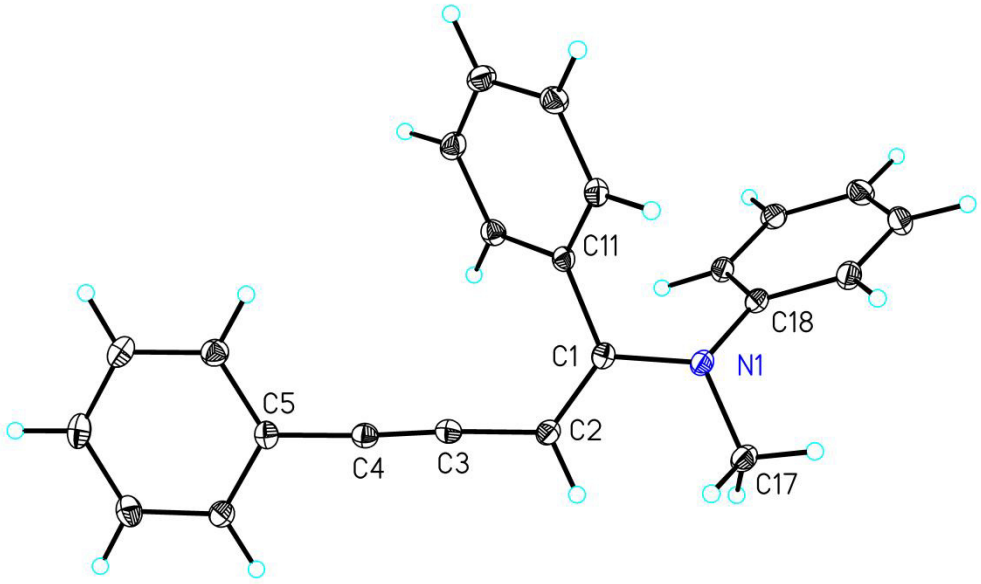


Figure 3.13: Molecular structure and numbering scheme of *E*-[**12**].The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii. Selected bond lengths and angles are listed in **Table 4**.

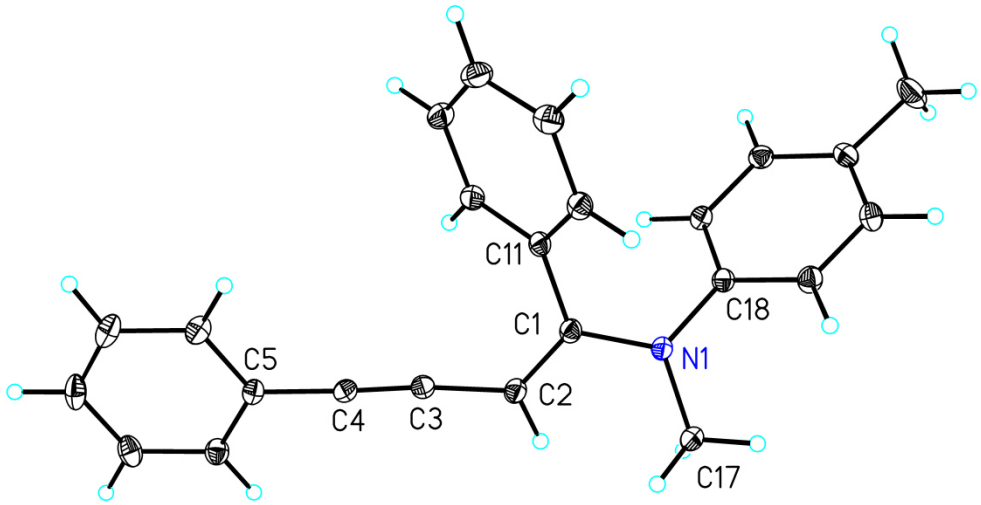


Figure 3.14: Molecular structure and numbering scheme of *E*-[**13**].The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii. Selected bond lengths and angles are listed in **Table 4**.

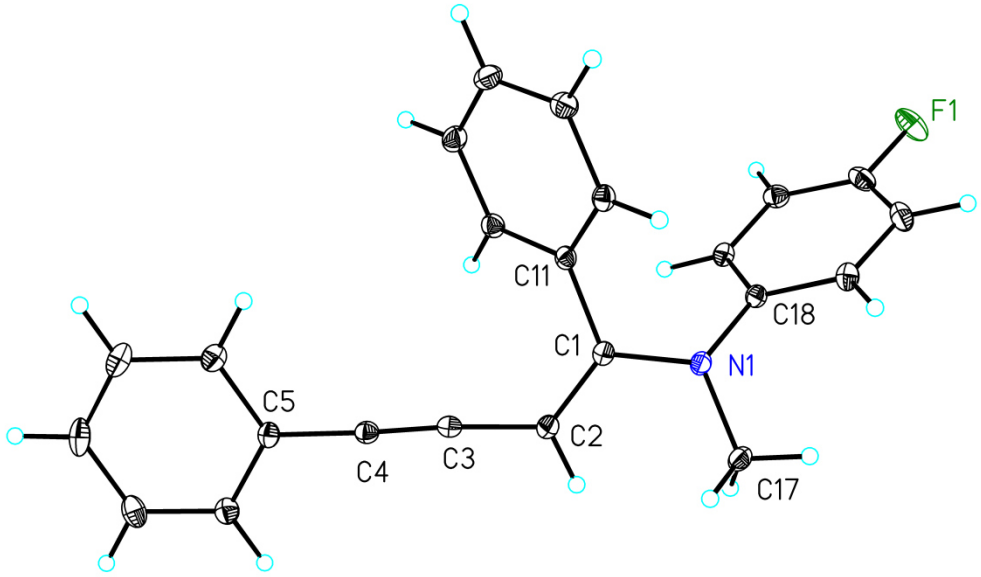


Figure 3.15: Molecular structure and numbering scheme of *E*-[**14**]. The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii. Selected structural parameters are listed in **Table 4**.

The molecular structure and numbering scheme of *E*-(1,4-diphenylbut-1-ene-3-yne-1-yl)-(4-fluorophenyl)-methylamine (*E*-[**14**]) is depicted in **Figure 3.15**. The essential structural parameters of *E*-[**12**], *E*-[**13**], and *E*-[**14**] are very similar and summarized in **Table 4**. The nitrogen atom N1 is in a nearly planar environment allowing conjugation of the lone pair with the but-1-ene- 3-yne unit. The N1-C17 and N1-C18 bond lengths represent characteristic N-C values to sp^3 and sp^2 hybridized carbon atoms, respectively. The shorter N1-C1 bond lengths hint toward a slight conjugation with the alkene moieties. The π-system of the alkene fragments do not interact with the adjacent phenyl group. The C1=C2 double bonds (135.3 to 135.8 pm) are only slightly elongated compared to the expected value of a double bond between sp^2 hybridized carbon atoms (134 pm).[183] The C3≡C4 triple bonds reflect the characteristic values of an isolated triple bond.

Table 4: Selected structural parameters (bond lengths [pm] and angles [deg.]) of the *E*-isomers *E*-[**12**], *E*-[**13**], and *E*-[**14**].

	E-[**12**]	*E*-[**13**]	*E*-[**14**]
N1-C17	146.78(16)	146.78(18)	146.76(13)
N1-C18	143.17(16)	143.10(17)	143.19(13)
N1-C1	139.99(15)	139.94(17)	139.97(13)
C1-C11	148.74(17)	149.09(18)	149.18(14)
C1-C2	135.33(17)	135.53(19)	135.77(15)
C2-C3	142.34(17)	142.29(19)	142.37(15)
C3-C4	120.27(18)	120.31(19)	120.40(15)
C4-C5	143.39(17)	143.38(19)	143.61(14)
C17-N1-C18	115.11(10)	115.06(11)	114.81(8)
C1-N1-C17	117.79(10)	117.88(11)	117.92(9)
C1-N1-C18	117.95(10)	119.37(11)	118.38(8)
N1-C1-C2	122.06(11)	121.07(12)	121.68(9)
N1-C1-C11	115.49(10)	115.49(11)	115.75(9)
C2-C1-C11	122.21(11)	123.22(12)	122.38(9)
C1-C2-C3	125.01(12)	126.78(13)	125.86(10)
C2-C3-C4	176.09(13)	173.87(14)	175.45(11)
C3-C4-C5	176.23(13)	177.59(14)	177.34(11)

Selected NMR data are summarized in **Table 5**. The numbering scheme for the carbon atoms is identical to the numbering of the X-ray structures discussed above. For the assignment, single crystals of the *E*-isomers were dissolved in an appropriate solvent and 2D-NMR experiments (H,H-COSY, HMBC and HSQC spectra) allowed an unambiguous assignment of these resonances, an assignment to specific carbon atoms was not possible. Thereafter, a mixture of both isomers allowed to assign also the resonances of the *Z*-isomers. The hydrogen atoms at the C2 atoms clearly allow to distinguish between the *E*- and *Z*-isomer because the resonances of the *E*-isomers are shifted toward a lower field by approx. $\Delta\delta = 0.5$ ppm. A comparable effect, albeit smaller, is also observed for the N-bound methyl groups. In the $^{13}C\{^{1}H\}$ NMR spectra only small differences of the chemical shifts of the isomers can be found.

Table 5: Selected NMR data of the singly hydroaminated diphenylbutadiyne. The numbering scheme is identical with the molecular structures and can be seen in Figure 3.13, Figure 3.14 and Figure 3.15

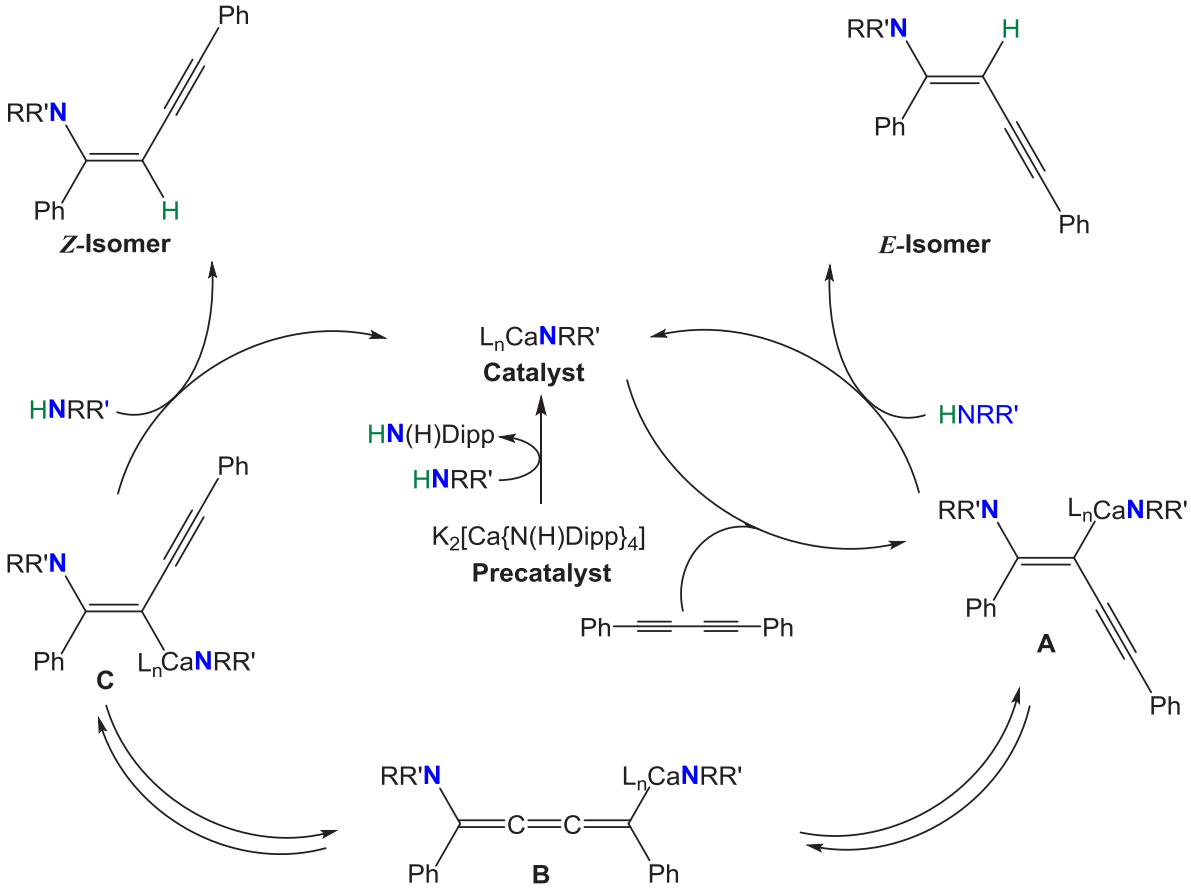
	E-[**12**]	*E*-[**12**]	*Z*-[**12**]	*E*-[**13**]	*Z*-[**13**]	*E*-[**14**]	*Z*-[**14**]
Solvent	DMSO	$[D_8]$THF	$[D_8]$THF	$[D_8]$THF	$[D_8]$THF	CD_2Cl_2	CD_2Cl_2
^1H							
C2-H	5.96	5.83	5.28	5.69	5.17	5.75	5.21
C17-H	3.34	3.40	3.25	3.42	3.26	3.40	3.23
$^{13}C\{^1H\}$							
C1	155.1	155.9	158.2	156.2	158.2	157.9	160.5
C2	99.9	100.3	90.6	88.8	87.5	88.3	88.9
C3	97.4	98.4	90.8 [a]	90.6 [a]	90.9 [a]	99.1	97.9
C4	88.3	88.6	91.1 [a]	91.1 [a]	90.1 [a]	90.5	90.4
C11	137.6	139.3	137.7	139.6	137.2	137.1	138.8
C17	39.4	39.5	41.5	40.0	42.2	41.6	39.7
C18	147.0	148.3	149.2	146.7	146.1	144.6	145.1

a) Assignment uncertain.

In contrast, no reactions were observed between *N*-methyl-4-(trifluoromethyl)aniline (**Figure 3.12**, **k**) and diphenylbutadiyne under the same reaction conditions (5 mol-% of the catalyst and 3 days stirring at room temperature). This secondary arylamine **k** is substituted with an electron withdrawing group ($-CF_3$) in *para*-position, which reduces the nucleophilicity by decreasing the electron density through the conjugated π-system of the aromatic ring from the nitrogen atom. Hence, no reactions could be occurred under the same conditions.

The reaction mechanism of the addition of the secondary arylamines across diphenylbutadiyne is less complicated than the addition of the primary arylamines, because the catalytic cyclization reactions are suppressed. In order to release steric pressure, which the precatalyst $[K_2Ca\{N(H)Dipp\}_4]$ ([**2**]) possess, at least one diisopropylanilide anion is exchanged by an *N*-methyl-arylamide through a transamination reaction, forming the catalytically active species yielding L_nCa-NRR' as shown in **Scheme 3.11**. L represents a Lewis base such as a solvent molecule (thf), an amine or an amide anion. The Ca-N bond adds to a C≡C triple bond leading to intermediate **A**. The newly formed and highly reactive

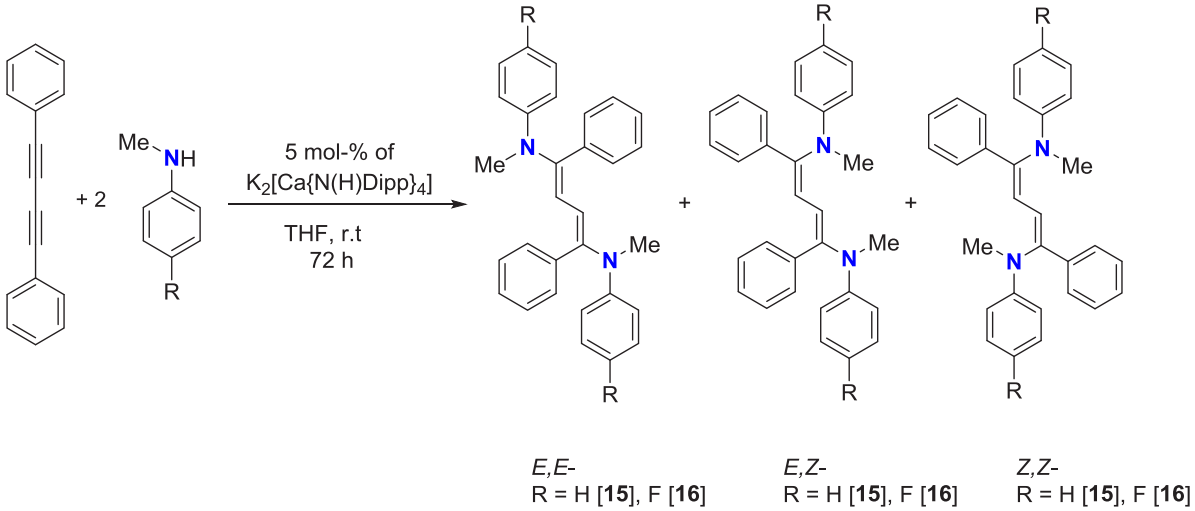
Ca-C moiety metalates an amine finally yielding the *E*-isomer and regenerating the catalyst. Even though the *E*-isomers represent the major product, significant amounts of the *Z*-isomers are observed. A 1,3-shift of the negative charge leads to the formation of cumulene **B** (which might also exist as a solvent-separated ion pair). From this isomer, the back reaction reforms isomer **A**, whereas also the other isomer **C** can be obtained. Metalation of the amine by **C** yields the *Z*-isomer (**Scheme 3.11**).



Scheme 3.11: Proposed catalytic cycle for the calcium-mediated hydroamination of diphenylbutadiyne (Ph = phenyl; R, R' = methyl aryl). Due to the fact that the exact composition of the catalytic species is unknown, the calcium catalyst is shown as [L_nCaNRR'] with L representing any Lewis base such as thf (solvent), amines and amides such as the anions NRR'^- and $N(H)Dipp^-$.

Doubly hydroaminated diphenylbutadiyne

The reaction of diphenylbutadiyne with two equivalents of *N*-methyl-aniline and *N*-methyl-4-fluoroaniline (**Figure 3.12**,**h, j**) after three days yielded an E/Z-isomeric mixture of 1,4-di(*N*-methyl-anilino)-1,4-diphenylbuta-1,3-diene [**15**] and 1,4-Diphenyl-1,4-bis(*N*-methyl-4-fluoroanilino)buta-1,3-diene [**16**], respectively as shown in **Scheme 3.12**.



Scheme 3.12: Synthesis of doubly hydroaminated diphenylbutadiyne.

The conversion was monitored by NMR spectroscopic measurements as depicted in **Figure 3.16**. These NMR studies showed that the formation of the *E*-isomer is favored, but again *cis*- and *trans*-addition was observed for the second hydroamination step, yielding *E*,*Z*- and *E*,*E*-1,4-di(*N*-methyl-anilino)-1,4-diphenylbuta-1,3-diene ([**15**]) as the major components. The *E*,*E*- and *Z*,*Z*-isomers are formed with a ratio of 3:1. This is in agreement with the formation of the singly hydroaminated compounds *E*-[**12**] and *Z*-[**12**] where the *E*-isomer also represents the favored product. The progress of the second hydroamination step can be elucidated from the resonances of the alkene protons in the region between δ = 5.3 and 7.0 ppm. The spectra were recorded after 1 h, 5 h, 21 h, 29 h, 59 h, and 72 h (**Figure 3.16**, from bottom to top) after mixing of the substrates. In the bottom spectrum *E*-[**12**] (δ = 5.82 ppm) and *Z*-[**12**] (δ = 5.28 ppm) are the major components; after 72 h, these compounds together with the doubly hydroaminated diphenylbutadiynes *E,E*-[**15**] (δ = 6.59 ppm), *E,Z*-[**15**] (δ =

5.93 and 6.7 ppm), and *Z,Z*-[**15**] (δ = 6.26 ppm) are observed, respectively. A complete conversion was not achieved under these reaction conditions. A final NMR experiment approximately after one-month reaction time still contained singly hydroaminated [**12**].

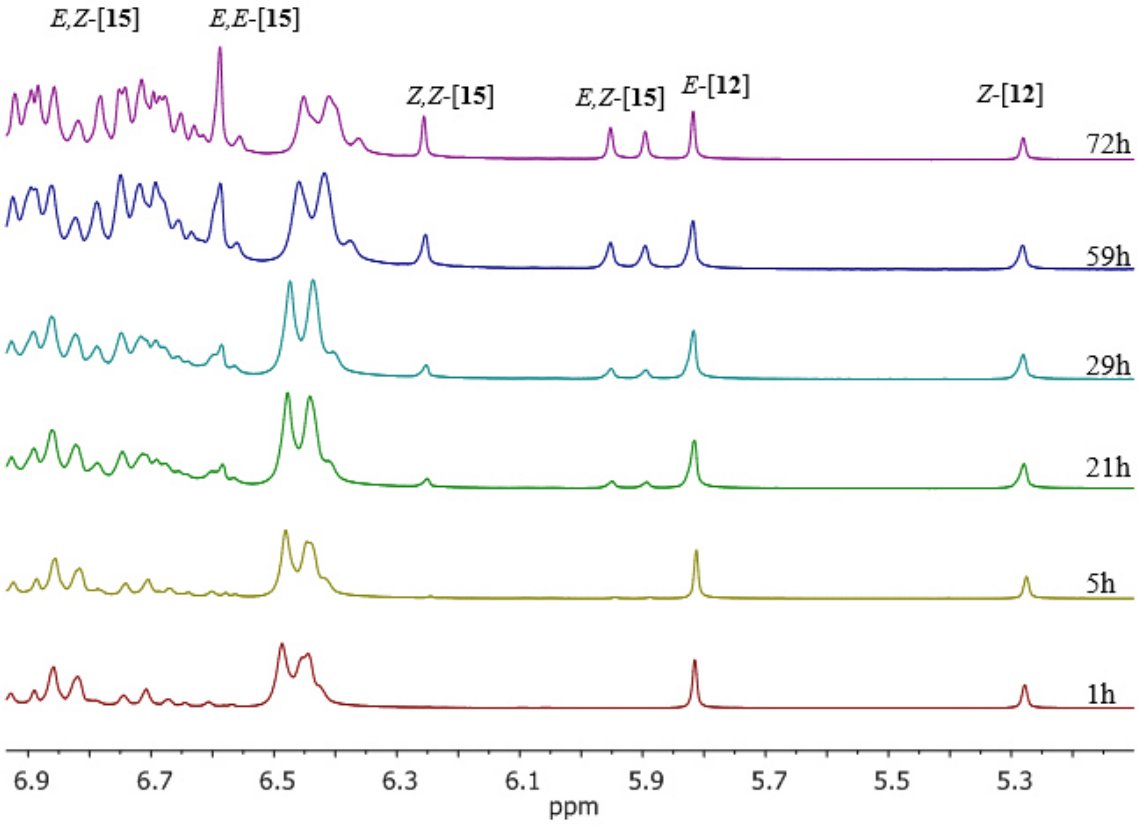


Figure 3.16: NMR spectroscopic monitoring of the second hydroamination of an *E*/*Z*-mixture of [**12**].

The time-dependent conversion of the singly hydroaminated diphenylbutadiyne [**12**] to the doubly hydroaminated derivatives [**15**] is depicted in **Figure 3.17**. The s-block metal-mediated hydroamination of the second C≡C triple bond of diphenylbutadiyne is significantly slower than the first hydroamination process, allowing the isolation of the pure mono-hydroamination product [**12**]. However, the mono-hydroaminated product was still present after several days or even weeks. Thus, the reaction solution showed a mixture of 10 % of *Z*-[**12**] and 20 % of *E*-[**12**] as well as 30-% of *E,E*-[**15**], 30 % of *E,Z*-[**15**] and 10 % of *Z,Z*-[**15**] after 72 hours.

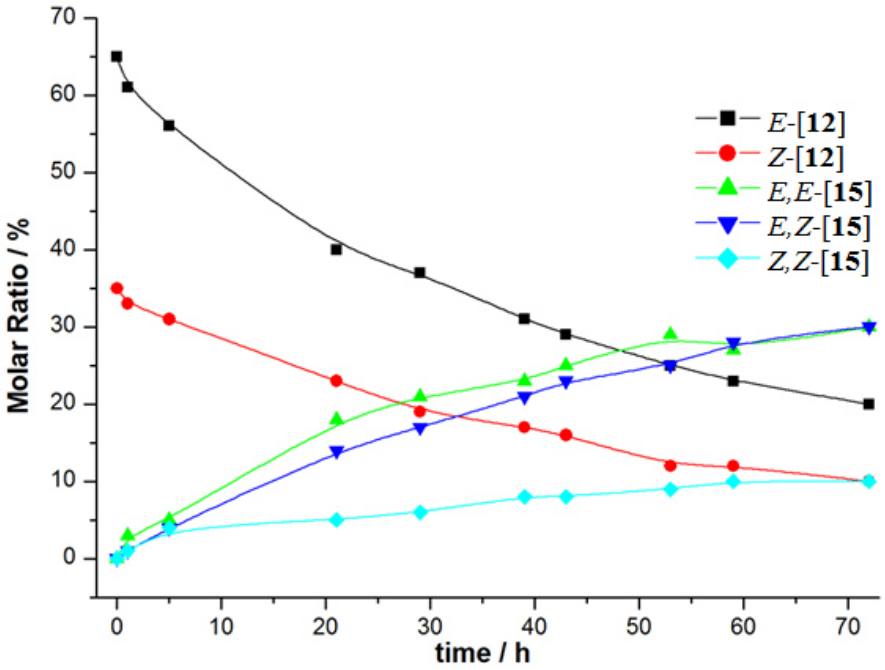


Figure 3.17: Time-dependent conversion of the singly hydroaminated compounds *E*-[**12**] and *Z*-[**12**] to the doubly hydroaminated isomer mixture [**15**] in the presence of 5 mol-% of catalytically active [$K_2Ca\{N(H)Dipp\}_4$] in THF at room temperature. Due to the fact that no side-products were formed during this s-block metal-mediated hydroamination all compounds add up to 100 %.

The bulkier *N*-methyl-p-toluidine (**Figure 3.12**, **i**) reacted only once, regardless of the applied stoichiometry giving exclusively the singly hydroaminated product [**13**] with the same ratio of *E*- and *Z*-isomers. In contrast to this inhibition by a *para*-methyl substituent, the hydroamination of diphenylbutadiyne with *N*-methyl-para-fluoroaniline (**Figure 3.12**, **j**) showed that the second hydroamination step also occurred readily leading to *E*/*Z*-mixtures of 1,4-di(*N*-methyl-para-fluoroanilino)-1,4-diphenylbuta-1,3-diene [**16**]. The reaction of 1-(*N*-methyl-anilino)-1,4-diphenylbut-1-ene-3-yne [**12**] with *N*-methyl-para-fluoroaniline led to the formation of the asymmetric 1,4-hydroaminated butadiene derivative [**17**]. Due to the lack of formation of symmetric [**15**] and [**16**], an equilibrium with amination-deamination pathways can be excluded. In contrast to these findings, *N*-methyl-toluidine again showed no tendency to react with the second C≡C triple bond of [**12**] under these reaction conditions.

The centrosymmetric molecular structures of the doubly hydroaminated isomers *E,E*-[**15**] and *Z,Z*-[**16**] are displayed in **Figure 3.18** and **Figure 3.19**, respectively.

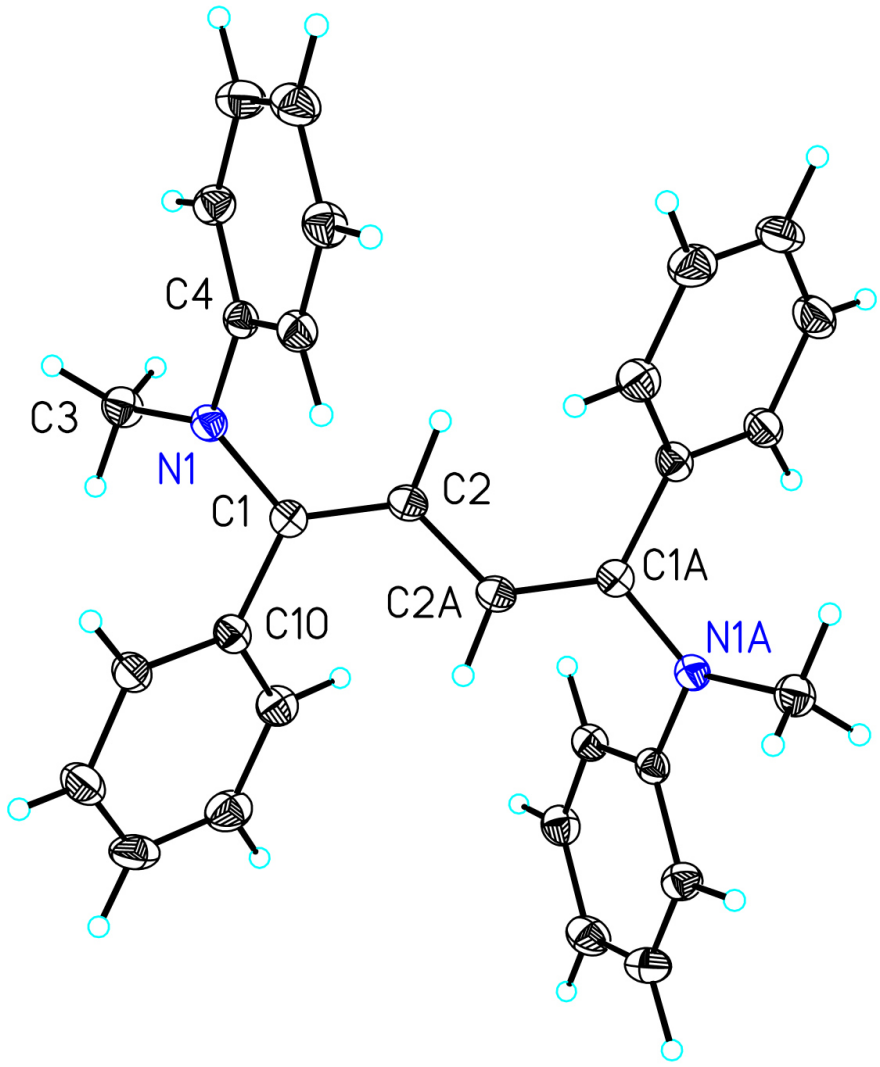


Figure 3.18: Molecular structure and numbering scheme of centrosymmetric *E,E*-[**15**]. Symmetry-related atoms are marked with the letter "A". The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected structural parameters are listed in **Table 6**.

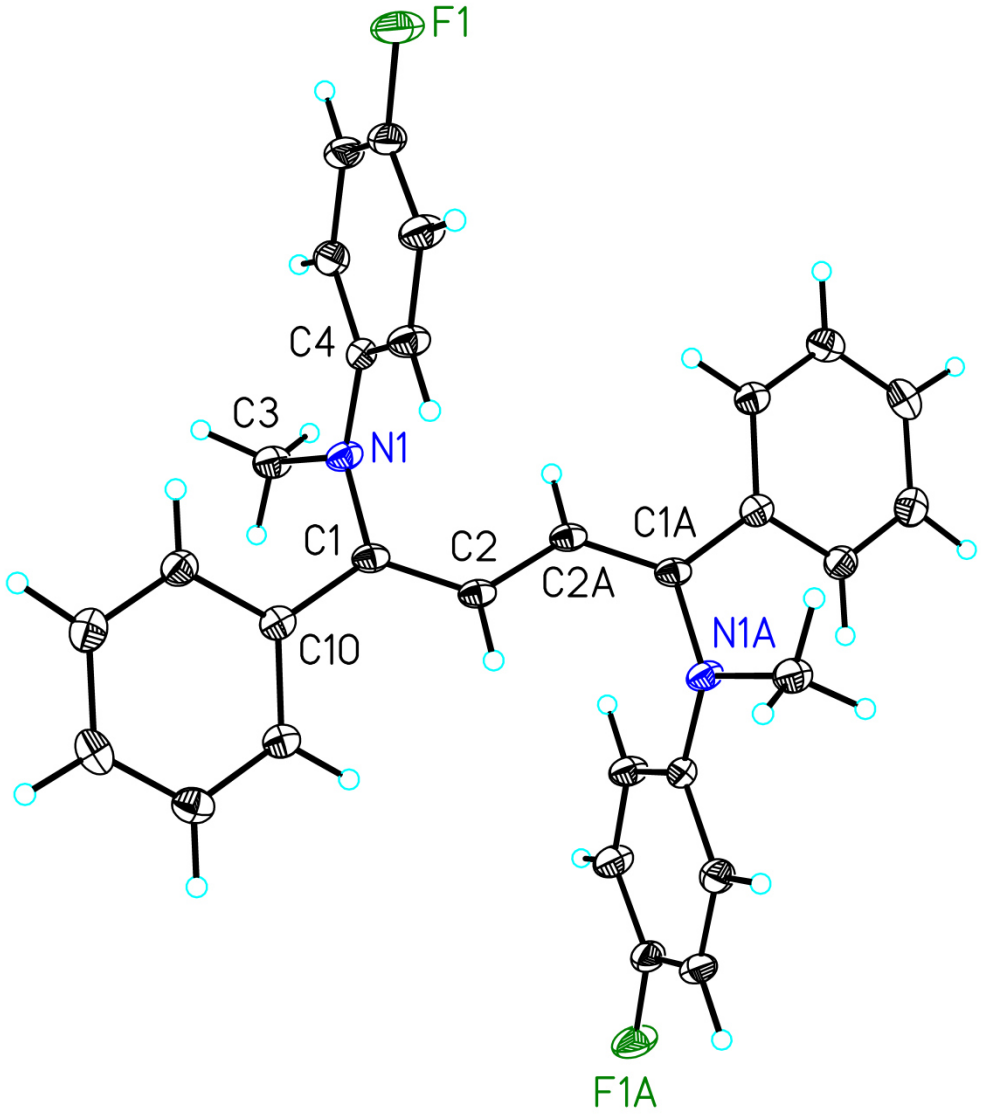


Figure 3.19: Molecular structure and numbering scheme of centrosymmetric *Z,Z*-[**16**]. Symmetry-related atoms are marked with the letter "A". The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii. Selected bond lengths and angles are summarized in **Table 6**.

The asymmetric derivative [**17**] crystallized as a *Z,Z*-isomer in the centrosymmetric monoclinic space group $P2_1/c$ with the center of symmetry on the butadiene unit leading to

1:1 disordering of the 4-fluorophenyl and the *N*-bound unsubstituted phenyl groups. In **Figure 3.20**, the C-F and C-H bonds to the disordered atoms with occupancy factors of 50 % are shown as broken lines; only one orientation of this molecule is depicted. Due to the fact that the influence of the *para*-positioned substituents on the structure of the central moieties is negligible in the singly hydroaminated derivatives ([**12**], [**13**] or [**14**]), their structural parameters are reliable. Selected structural data are summarized in **Table 6**.

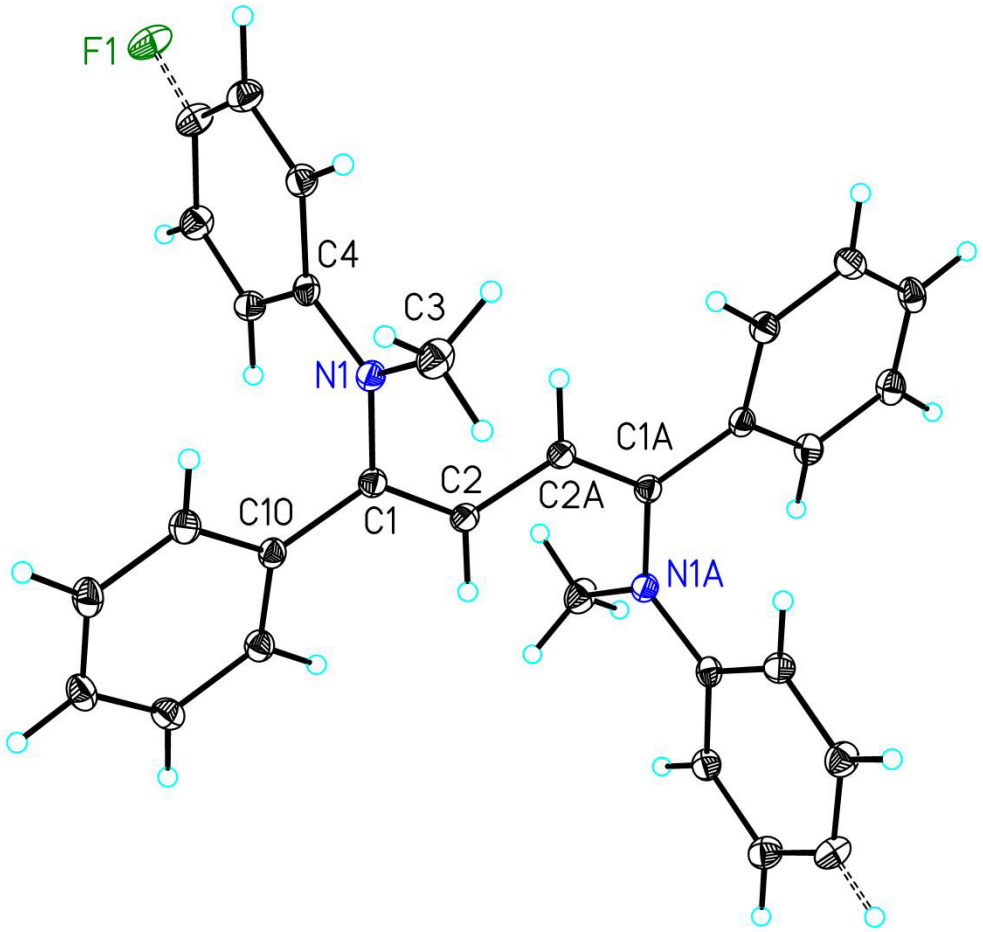


Figure 3.20: Molecular structure and numbering scheme of *Z,Z*-[**17**]. Symmetry-related atoms are marked with the letter "A". Due to the centro-symmetry the fluorine and hydrogen atoms at C7 (the respective bonds are depicted as broken lines) is disordered with a 1:1 ratio, only one orientation is depicted in this figure. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii.

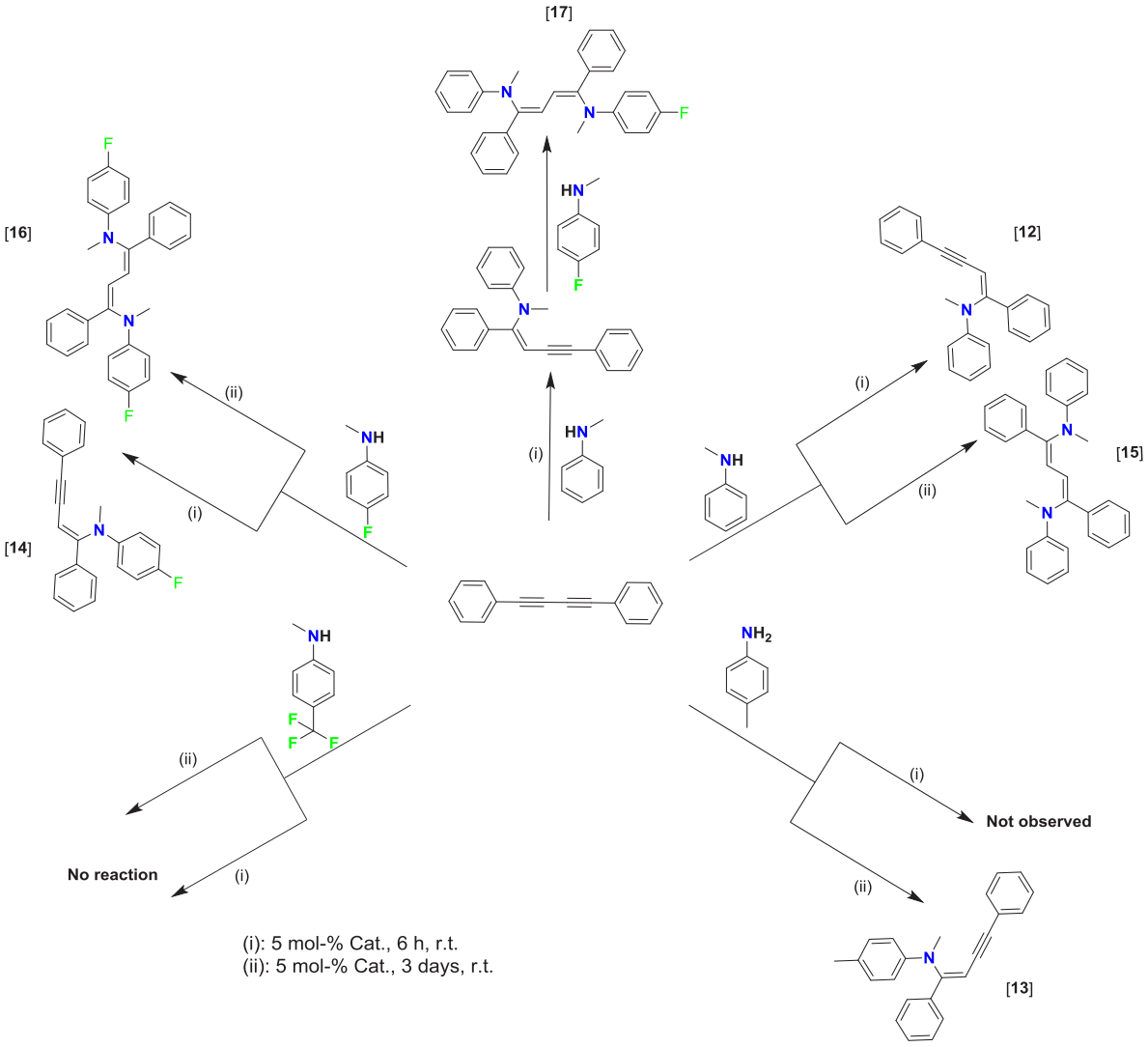
The central butadiene units resemble characteristic bond lengths of C-C single and C=C double bonds without significant charge delocalization. In agreement with this interpretation, the C1-C10 bond lengths to the phenyl groups resemble characteristic single bond values between sp^2 hybridized carbon atoms.[183] Due to the crystallographic inversion symmetry, the buta-1,3-diene units are strictly planar. According to the VSEPR concept multiple bonds are more demanding than single bonds and therefore, they require more space leading to decreased N1-C1-C11 bond angles.

Table 6: Selected structural parameters (bond lengths [pm] and angles [°]) of doubly hydroaminated diphenylbutadiyne.

	E,E-[**15**]	*Z,Z*-[**16**]	*Z,Z*-[**17**]
N1-C4	141.9(3)	139.5(3)	139.2(3)
N1-C3	146.2(3)	146.0(3)	145.7(3)
N1-C1	141.4(3)	143.1(3)	142.9(2)
C1-C10	148.3(4)	147.7(4)	148.1(3)
C1-C2	136.0(4)	135.1(4)	135.1(3)
C2-C2A	143.8(5)	143.8(5)	144.3(4)
C3-N1-C4	116.9(2)	119.0(2)	119.8(2)
C1-N1-C3	117.6(2)	117.0(2)	118.6(2)
C1-N1-C4	120.8(2)	121.5(2)	121.5(2)
C2-C1-C10	123.8(2)	122.0(2)	122.4(2)
N1-C1-C10	115.1(2)	117.2(2)	117.5(2)
N1-C1-C2	121.1(2)	120.8(2)	119.8(2)
C1-C2-C2a	126.6(3)	125.5(3)	125.0(2)

In the *E*-isomeric mono-hydroamination products [**12**] to [**14**], the N-C bond to the butadiene fragment is shorter than the bond to the aryl group. This trend is also realized in the doubly hydroaminated *E,E*-isomeric derivatives. In the *Z,Z*-isomers [**16**] and [**17**], a characteristic N1-C1 single bond is observed whereas a shortening of the N1-C4 bond to the adjacent aryl group resembles a slight interaction between the lone pair at N1 and the π-system of this aryl group. In *E,E*-isomeric [**15**] the N1-C1 and N1-C4 bond lengths show very similar values with a smaller degree of charge delocalization. This finding verifies that the direction of the small contributions of π-interaction is dictated by the minimization of steric pressure within the molecules.

In summary, the precatalyst [$K_2Ca\{N(H)Dipp\}_4$] ([**2**]) was employed to study the hydroamination of diphenylbutadiyne with secondary *N*-methyl-arylamines in tetrahydrofuran at room temperature. After approximately 6 h a nearly complete conversion with a catalyst loading of 5 mol-% led to singly hydroaminated butadiyne (conditions (i) in S**cheme 3.13**). The second hydroamination step of the other C≡C triple bond requires much longer time at similar reaction conditions (conditions (ii) in **Scheme 3.13**). After three days mixtures of singly and doubly hydroaminated diphenylbutadiyne were obtained if *N*-methylaniline and *N*-methyl-4-fluoroaniline were employed. In contrast, no significant amounts of doubly hydroaminated diphenylbutadiyne was observed for the hydroamination with *N*-methyl-4-tolylamine.

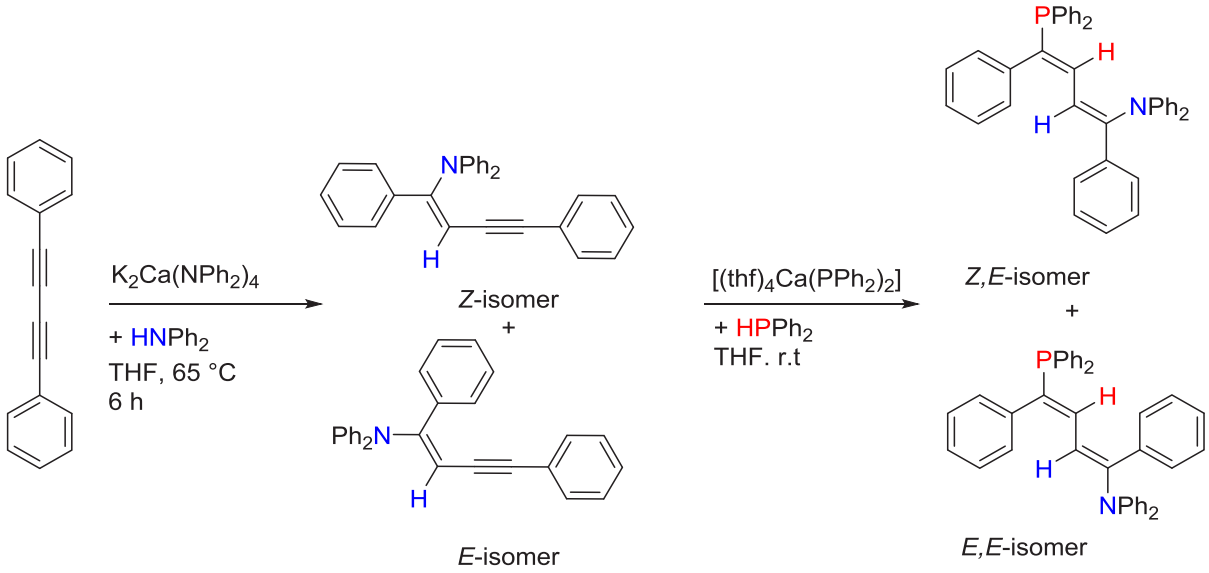


Scheme 3.13: Addition of secondary arylamines across diphenylbutadiyne under two different reaction conditions ((i) and (ii)).

This work was published in 2016.[184]

3.2.3 Addition of diphenylphosphane

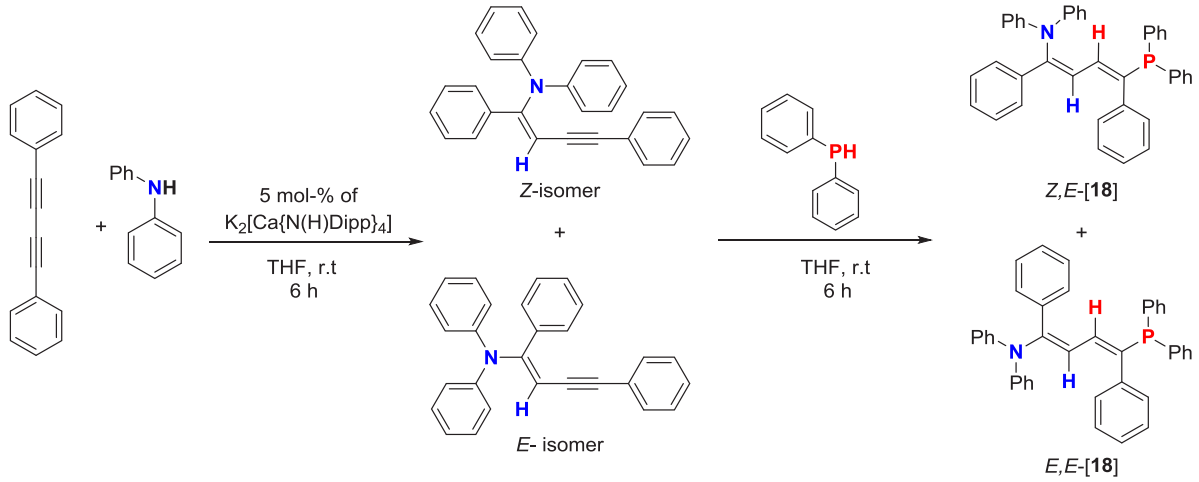
In 2012 *GLOCK* et al. synthesized the singly hydroaminated *E*- and *Z*-isomers of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne via reacting diphenylbutadiyne with diphenylamine in the presence of $[K_2Ca(NPh_2)_4]$ as catalyst in boiling THF for 6 hours. In this reaction the high temperature was required for enhancement of the catalyst reactivity and, hence, the conversion of the products.[162c] Afterwards these products were hydrophosphanylated with diphenylphosphane in tetrahydrofuran in the presence of 5 mol-% of $[(thf)_4Ca(PPh_2)_2]$ quantitatively yielding 1-diphenylamino-1,4-diphenyl-4-diphenylphosphanylbuta-1,3-diene by *WESTERHAUSEN* et al.[185] The *E/Z*-isomerism at the amino functionality is maintained, whereas only the *E*-isomeric hydrophosphanylation was observed according to **Scheme 3.14**.



Scheme 3.14: Two-step synthesis of 1-(diphenylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene using different calcium-based catalysts for the hydropentelation reactions.

These findings suggest that the synthesis of substituted 1-amino-4-phosphanylbuta-1,3-dienes requires the hydroamination as the initial step and the hydrophosphanylation as a subsequent reaction.

In order to study the reactivity of the calciate precatalyst [**2**] in the hydrophosphanylation reactions and hence the elimination of the necessity to change the calcium-based catalyst from the $K_2Ca(NHRR`)_4$ for the hydroamination to $[(thf)_4Ca(PPh_2)_2]$ for the subsequent hydrophosphanylation step, we repeated this catalytic hydrophosphanylation of 1-(diphenylamino)-1,4-diphenylbut-1-ene-3-yne by using catalytic amounts of $K_2[Ca\{N(H)Dipp\}_4]$ ([**2**]). After complete conversion, the solvent was removed and the residue dissolved in methanol to inactivate the calcium catalyst. After removal of methanol, the residue was dissolved in methylene chloride and filtered to remove the calcium-containing compounds. Thereafter, recrystallization from methylene chloride/pentane again provided yellow crystals of *E/E*-[**18**] and *Z/E*-[**18**] as shown in **Scheme 3.15**.



Scheme 3.15: Hydroamination and hydrophosphanylation of diphenylbutadiyne provided by $K_2[Ca\{N(H)Dipp\}_4]$.

This result suggests that the two different hydroelementation reactions could be performed without a change of the catalyst system and without the need to isolate the hydroamination product prior to the hydrophosphanylation reaction.

The structural elucidation of the compositions of *E,E*-[**18**] and *E,Z*-[**18**] succeeded by X-ray diffraction experiments at single crystals. Molecular structures and numbering schemes of *E,E*-[**18**] and *Z,E*-[**18**] are presented in **Figure 3.21** and **Figure 3.22**, respectively. Selected structural parameters are summarized in **Table 7**.

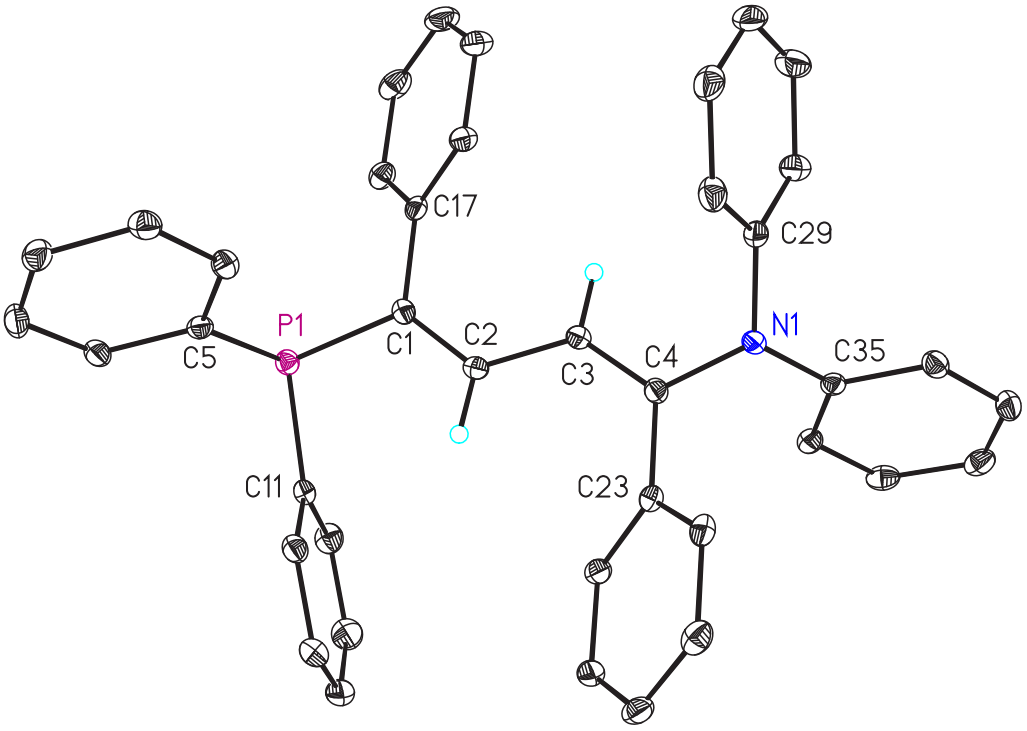


Figure 3.21: Molecular structure and numbering scheme of (*E,E*)-1-diphenylphosphanyl-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene (*E,E*-[**18**]). The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii.

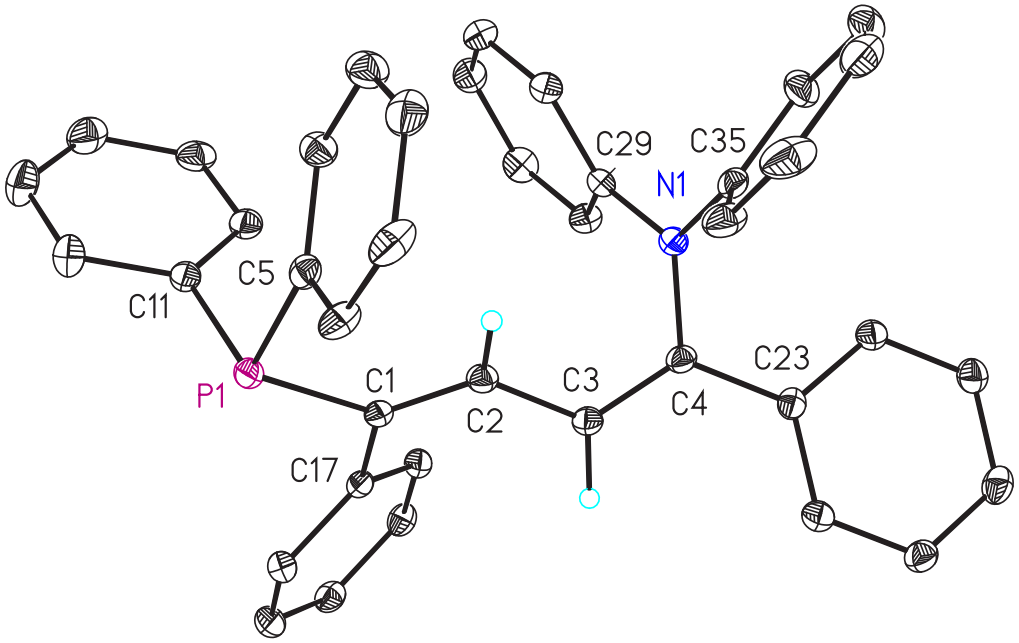
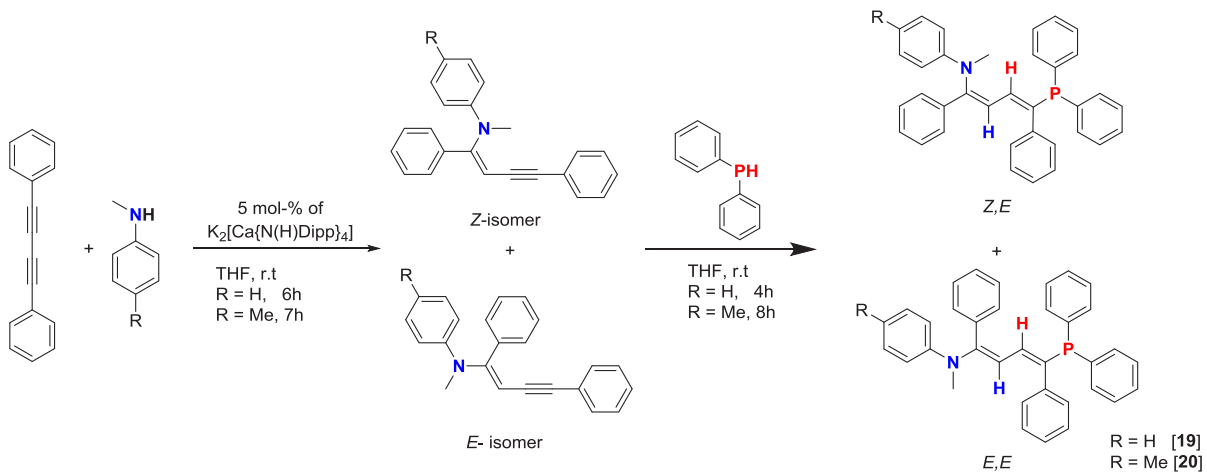


Figure 3.22: Molecular structure and numbering scheme of (*E,Z*)-1-diphenylphosphanyl-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene (*E,Z*-[**18**]). The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii.

In order to ensure our finding, that the hydrophosphanylation occurs regio- and stereoselective to the *E*-isomeric hydrophosphanylation products, we investigated our singly hydroaminated products 1-(*N*-methyl-anilino)-1,4-diphenylbut-1-ene-3-yne ([**12**]) and 1-(*N*-methyl-tolylamino)-1,4-diphenylbut-1-ene-3-yne ([**13**]) in hydrophosphanylation reactions. Under the same conditions which have been employed to synthesize 1-(diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene [**18**], diphenylphosphane was added to this reaction mixture, yielding the appropriate hydrofunctionalization products 1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-anilino)buta-1,3-diene [**19**] and 1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-tolylamino)buta-1,3-diene [**20**] according to **Scheme 3.16**. Again, the initial hydroamination reaction gave an *E/Z*-isomeric mixture, whereas the hydrophosphanylation occurred regio- and stereoselective to the *E*-isomeric hydrophosphanylation products.



Scheme 3.16: Calcium-mediated synthesis of 1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methylanilino)buta-1,3-dienes (R= H [**19**], Me [**20**]).

Isolation of the intermediate hydroamination products 1-amino-1,4-diphenylbut-1-ene-3-yne proved to be advantageous in order to prevent impurities of bis-hydroaminated compounds. Unreacted butadiyne also has to be removed prior to the hydrophosphanylation procedures, otherwise the product contained bis-hydrophosphanylated derivatives as well. These side-products hamper the isolation of analytically pure 1-(diphenylphosphanyl)-1,4-diphenyl-4-(amino)buta-1,3-diene and, hence, lower the yields. Therefore, the preferred method involves an initial hydroamination reaction, catalyzed by $K_2[Ca\{N(H)Dipp\}_4]$ ([**2**]), followed by isolation and purification of 1-amino-1,4-diphenylbut-1-ene-3-yne. Thereafter, the hydrophosphanylation of this amine led to *E,Z*- and *E,E*-isomeric 1-(diphenylphosphanyl)-1,4-diphenyl-4-(amino)buta-1,3-dienes. This finding is most probably the consequence of steric strain but electronic effects may also play a minor role. Verification of the compositions [**19**] and [**20**] succeeded also by X-ray diffraction experiments at single crystals. Molecular structures and numbering schemes of *E,Z*-[**19**], *E,E*-[**20**] are presented in **Figure 3.23** and **Figure 3.24**, respectively. Selected structural parameters are summarized and compared in **Table 7**.

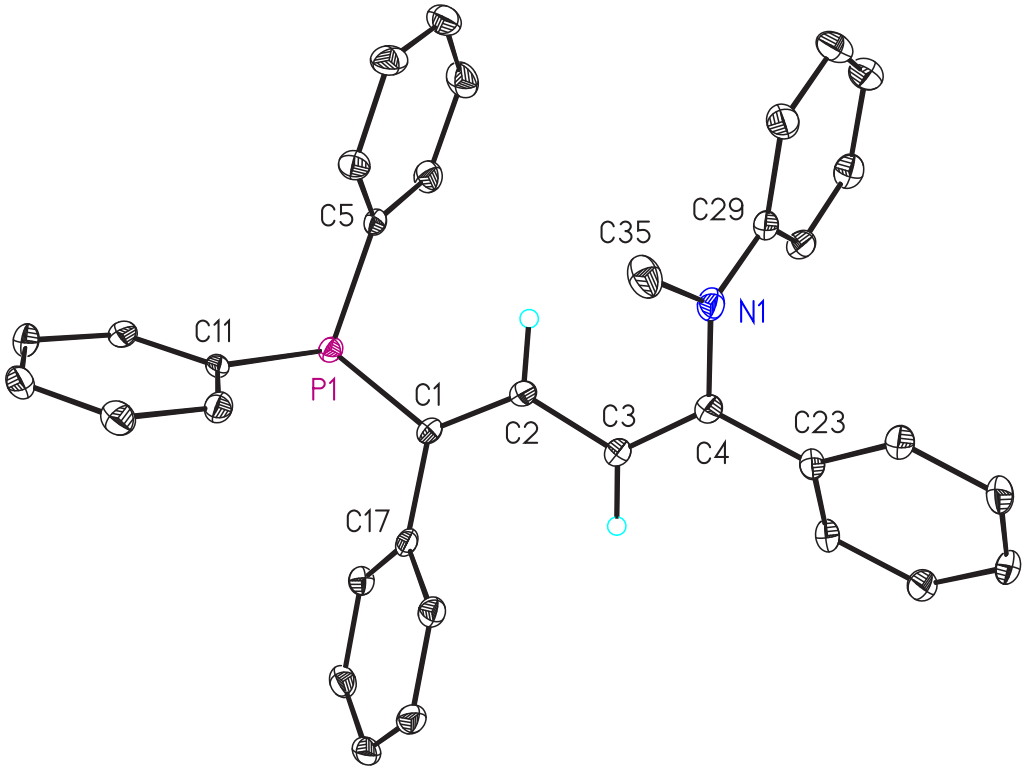


Figure 3.23: Molecular structure and numbering scheme of (*E,Z*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-anilino)buta-1,3-diene (*E,Z*-[**19**]). The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii.

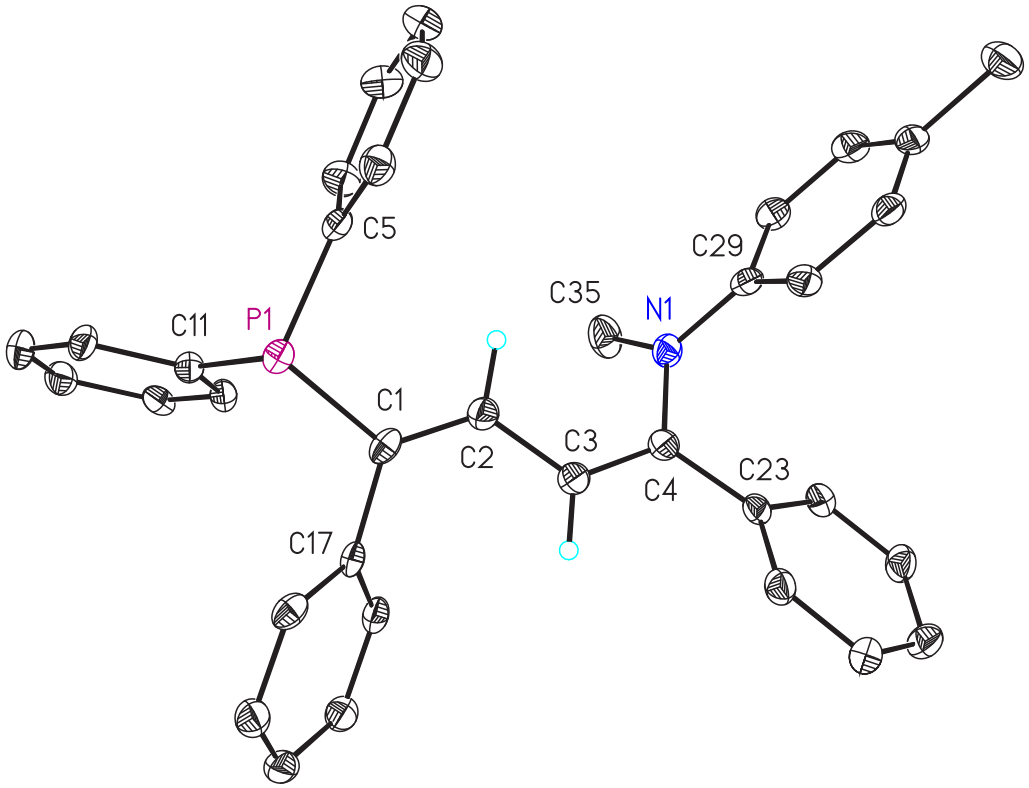


Figure 3.24: : Molecular structure and numbering scheme of (*E,Z*)1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-tolylamino)buta-1,3-diene (*E,Z*-[**20**]). The ellipsoids represent a probability of 30 %, H atoms are drawn with arbitrary radii.

The molecular structures of (*E,E*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene (*E,E*-[**18**]), (*E,Z*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene (*E,Z*-[**18**]), (*Z,E*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-anilino)buta-1,3-diene (*Z,E*-[**19**]) and (*E,Z*)1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-tolylamino)buta-1,3-diene (*E,Z*-[**20**]) show regardless of the isomerism high similarities. Selected structural parameters are compared in **Table 7**. The butadiene fragment shows no delocalization, typical C=C and C-C bond lengths of approximately 135 and 145 pm, respectively, are observed. Due to steric reasons, the planar amino group is twisted toward the planar butadiene plane and therefore, the electron pair with N cannot interact with the π-system of the butadiene moiety. In contrast to the amino group, the phosphorus atom is in a trigonal pyramidal environment with C-P-C bond angles of about 102°. Steric strain between the substituents in 1- and 4-position leads to a distortion

of the C-C-C bond angles of the butadiene fragment. The C1-C2-C3 and C2-C3-C4 bond angles of *E,E*-[**18**] are both significantly widened whereas for all *E,Z* isomers the enhancement of these bond angles are smaller. This fact verifies a smaller intramolecular steric strain for the *E,Z* isomers than for the *E,E* derivatives. Lack of interaction between the phosphanyl- end groups and the butadiene units leads to very similar P-C bonds of approximately 183 pm to the phenyl and butadiene moieties in all these compounds representing a characteristic P-C single bond value.

Table 7: Selected structural parameters of (*E,E*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene (*E,E*-[**18**]), (*E,Z*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene (*E,Z*-[**18**]), (*Z,E*)-1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-anilino)buta-1,3-diene (*Z,E*-[**19**]) and (*E,Z*)1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-tolylamino)buta-1,3-diene (*E,Z*-[**20**]).

	E,E-**18**	*E,Z*-**18**	*E,Z*-**19**	*E,Z*-[**20**]
P1-C1	182.9(2)	183.6(2)	183.5(3)	182.7(4)
C1-C2	135.5(3)	134.6(2)	135.2(4)	134.0(6)
C2-C3	144.6(3)	145.0(2)	144.7(4)	144.8(6)
C3-C4	134.9(3)	135.3(2)	135.1(4)	135.6(6)
N1-C4	143.3(3)	142.3(2)	142.0(4)	141.4(5)
P1-C5	182.0(3)	183.6(2)	183.4(3)	182.9(5)
P1-C11	182.3(3)	182.9(2)	183.8(2)	182.9(4)
C1-C17	148.4(3)	148.4(2)	149.3(4)	149.6(6)
C4-C23	148.7(4)	147.6(2)	148.7(4)	148.0(6)
N1-C29	143.5(3)	141.5(2)	139.5(4)	141.2(6)
N1-C35	142.9(3)	142.6(2)	146.1(4)	145.0(6)
C1-P1-C5	102.1(1)	102.10(8)	102.2(1)	103.6(2)
C1-P1-C11	102.7(1)	102.11(8)	103.8(1)	102.7(2)
C5-P1-C11	103.9(1)	102.44(8)	102.5(1)	103.3(2)
P1-C1-C2	122.1(2)	121.7(1)	121.8(2)	123.0(3)
C1-C2-C3	125.2(2)	127.7(2)	126.9(3)	126.5(4)
C2-C3-C4	127.1(2)	122.3(2)	122.1(3)	124.8(4)
C3-C4-N1	118.8(2)	118.8(2)	120.7(2)	120.0(4)
C4-N1-C29	117.3(2)	120.1(1)	120.4(2)	120.8(3)
C4-N1-C35	117.7(2)	119.5(1)	119.5(3)	119.0(4)
C29-N1-C35	118.8(2)	120.1(1)	119.9(3)	118.8(4)

Selected NMR parameters of the 1-(diphenylphosphanyl)-1,4-diphenyl-4-(amino)buta-1,3-dienes are compared in **Table 8**. The *E*/*Z*-isomerism of the amino group has a small influence on the chemical shifts of the ^{31}P nuclei. Thus, the ^{31}P resonances of the *E,E* isomers are observed at nearly +5 ppm whereas the *Z,E* isomers show chemical shifts of about +2.5 ppm. The carbon atoms of the butadiene backbone show low field shifted signals between 135 and 156 ppm. Here, the amino-substituted C4 atoms lie at lower field than the *P*-bound carbon atoms C1. The absolute values of the $^{n}J_{C,P}$ coupling constants decrease with increasing n from approximately 22 Hz (n = 1) over 12 Hz (n = 2) to 2 Hz (n = 3). The vicinal $^{3}J_{H,H}$ and $^{3}J_{H,P}$ couplings of the hydrogen atoms at C2 and C3 also depend on the isomerism of the amino group with larger values for the *E,E*-isomers.

Table 8: Selected NMR data of the *E,E* and *E,Z* isomers of 1-(diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene ([**18**]), 1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-anilino)buta-1,3-diene ([**19**]), and 1-(diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-tolylamino)-buta-1,3-diene ([**20**]).

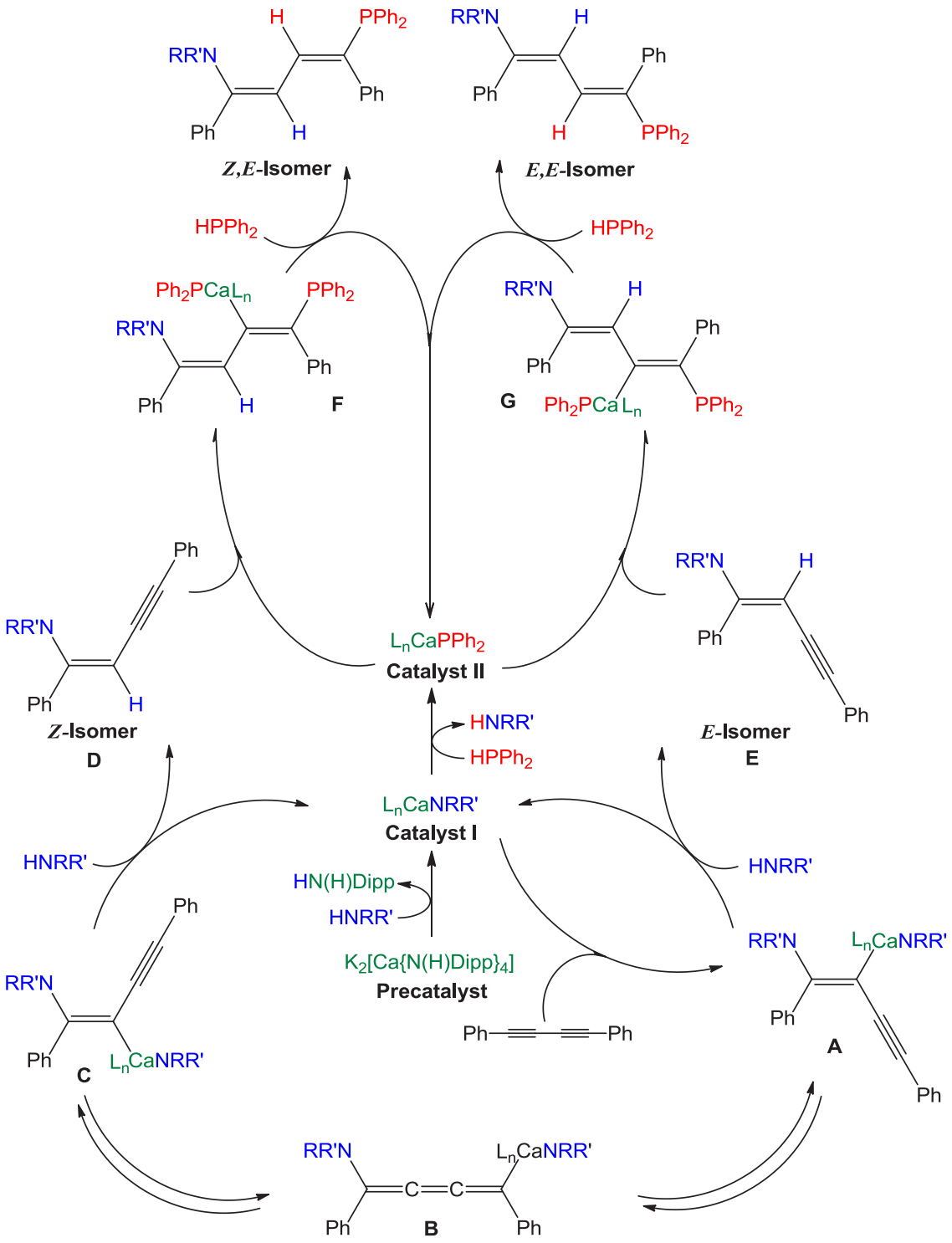
	E,E-[**18**]	*Z,E*-[**18**]	*E,E*-[**19**]	*Z,E*-[**19**]	*E,E*-[**20**]	*Z,E*-[**20**]
			^{1}H NMR			
δ(C2-*H*)	6.39	6.29	6.27	6.01	6.31	6.03
δ(C3-*H*)	6.62	6.45	6.49	6.51	6.49	6.42
^{3}J(H,H)	8.3	5.3	8.2	5.9	8.5	6.0
^{3}J(H,P)	12.1	10.7	11.6	10.9	11.5	10.9
δ(N-C*H*$_3$)	-	-	3.04	2.82	2.96	2.81
			^{13}C{^{1}H} NMR			
δ(*C*1)	140.6	140.4	141.8	141.1	140.3	142.4
^{1}J(C,P)	23.1	23.1	19.8	22.1	22.2	22.7
δ(*C*2)	136.4	135.0	136.2	136.2	136.1	135.5
^{2}J(C,P)	11.7	12.1	12.3	12.3	10.8	12.4
δ(*C*3)	146.7	145.7	147.5	147.5	146.6	147.0
^{3}J(C,P)	2.5	2.1	2.1	2.1	2.8	2.2
δ(*C*4)	147.5	147.1	151.6	149.5	152.0	156.0
^{4}J(C,P)	-	-	-	-	-	-
δ(N-*C*H$_3$)	-	-	40.9	38.1	38	37.5
			^{31}P{^{1}H} NMR			
δ(*P*1)	4.45	2.54	4.70	2.28	4.96	2.35

In agreement with the structural data, the *E,Z*-isomeric forms are the major components, whereas the amount of the *E,E* isomers is always significantly smaller. Therefore, we were

able to isolate and crystallize the *E,Z* isomers of all reported derivatives, whereas the parameters of the *E,E*-isomeric compounds had to be elucidated from isomeric mixtures.

Proposed Mechanism

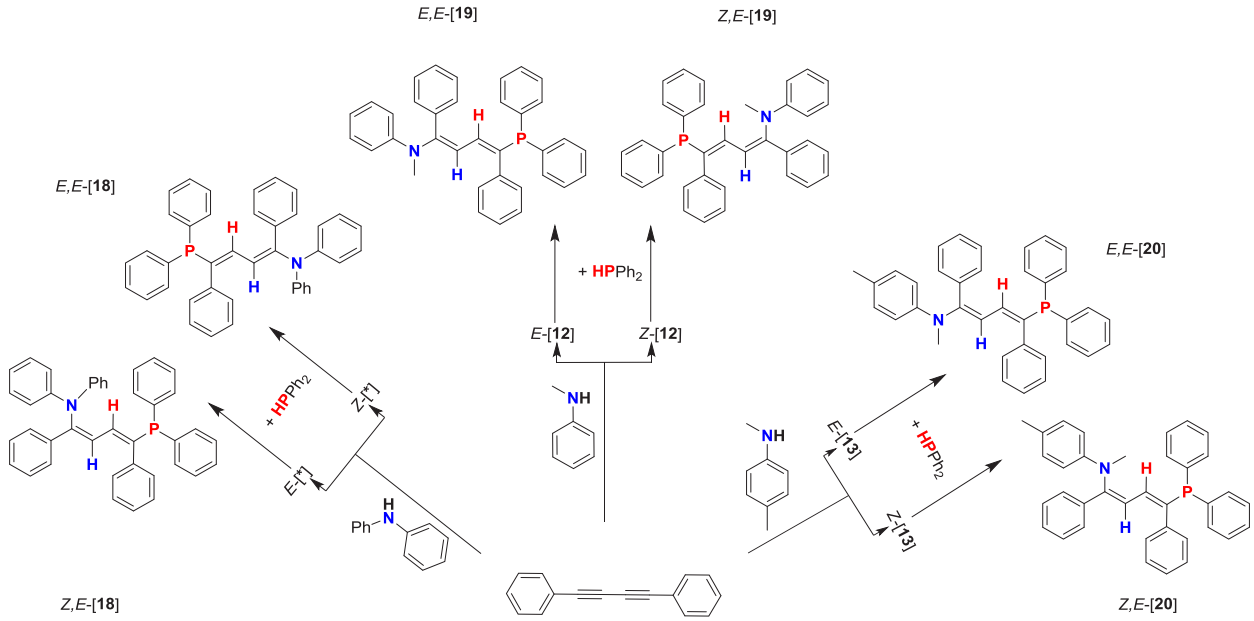
Based on these observations, the catalytic cycle has to be formulated as a two-step reaction sequence and the proposed mechanism is presented in **Scheme 3.17**. The initial catalytic cycle is depicted in the bottom part of this scheme. After addition of the Ca-N bond, the intermediately formed alkenylcalcium complex **A** either deprotonates an amine (formation of the *E*-isomeric alkenylamine) or rearranges via the intermediates **B** and **C** to the finally formed *Z*-alkenylamine. The necessity to obtain these singly hydroaminated products **D** and **E** limits the substitution pattern of the secondary amine substrates. For more reactive amines the second calcium-mediated hydroamination of the other C≡C triple bond overlaps with the first hydroamination step yielding mixtures of starting butadiyne, singly and doubly hydroaminated butadienes. In our hands, the above utilized aniline derivatives represent the preferred substrates.[184] After complete conversion and preferably isolation of the alkenylamines, diphenylphosphane is added, immediately yielding the catalytically active calcium phosphanide species (L represents Lewis bases such as anionic amides and phosphanides or neutral amines, phosphanes, or ethers). The addition of the newly formed Ca-P bond to the remaining C≡C triple bond yields the intermediates **F** and **G** that immediately deprotonate still present diphenylphosphane. This hydrophosphanylation always leads to the formation of *E*-isomeric alkenylphosphanes as shown in **Scheme 3.17**. In contrast to the calcium-mediated hydroamination, the catalytic hydrophosphanylation represents a very fast addition of a phosphane to an alkyne moiety. Under these reaction conditions neither the amines nor the phosphanes react with the C=C double bonds. The sequence of the catalytic steps (at first hydroamination, then hydrophosphanylation) must be maintained because otherwise the phosphanes always add quantitatively to both C≡C triple bonds yielding invariably doubly hydrophosphanylated derivatives regardless of the applied stoichiometry.[51a]



Scheme 3.17: The proposed catalytic cycles shown as a two-step process of subsequent hydroamination and hydrophosphanylation reactions. The bottom part shows the hydroamination and offers an explanation for the *Z*/*E*-isomerism. In the second hydrophosphanylation catalysis, the H-P bond adds to the second alkyne unit. The thus formed Ca-P bond adds to the remaining alkyne moiety followed by a metalation reaction.

L represents a Lewis base such as amido- or phosphanido- anions or neutral Lewis bases such as ethers, amines and phosphanes.

In summary, 1-phosphanyl-/ 4-amino-substituted buta-1,3-dienes can be prepared and isolated with moderate to good yields from a calcium-mediated step-wise addition of secondary arylamines and phosphanes to butadiyne. Both of these hydrofunctionalization reactions can be promoted with the coligand-free calciate $K_2[Ca\{N(H)Dipp\}_4]$ ([**2**]). Both hydroelementation steps are regioselective but only the catalytic addition of the H-P bond also stereoselectively yields the *E* isomer as shown in **Scheme 3.18**.



Scheme 3.18: Addition of diphenylphosphane to the singly hydroaminated molecules, [**12**], [**13**] and [*]. [*] is 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne.

This work was published in 2016.[186]

4 Summary and perspective (English version)

This thesis confirms that the addition reactions of various primary and secondary amines (hydroamination) as well as diphenylphosphane (hydrophosphanylation) across the C≡C triple bonds of diphenylbutadiyne can efficiently be catalyzed by a calciate complex. This calciate catalyst is a rival to the previously reported catalysts, such as those of d-orbital metals, lanthanoides and actinoides, which are mentioned in the introduction of the thesis. Importantly, the hydroamination and hydrophosphanylation reactions take place regioselectively whereas the latter occurs in a stereoselective manner. At the beginning of this work we were focusing on the modification of the complex-hexamethyldisilazide $[(L)_2Ca\{N(SiMe_3)_2\}_2]$ regarding to the coligand L and the possibility to apply the modified complex as catalyst. However, the latter complex for L = thf and L = thp was not sufficient to catalyze hydroamination reactions of diphenylbutadiyne with primary or secondary arylamines. The halide-free tetrahydropyran adduct $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ ([**1**]) is easily available in single-crystalline form via transmetalation of tin(II)-*bis*[bis(trimethylsilyl)amide] with calcium metal and subsequent recrystallization from *n*-hexane. This colorless complex shows good solubility in common organic solvents. The molecular structure is dominated by steric factors as also observed for adducts of CaI_2 and arylcalcium iodides.

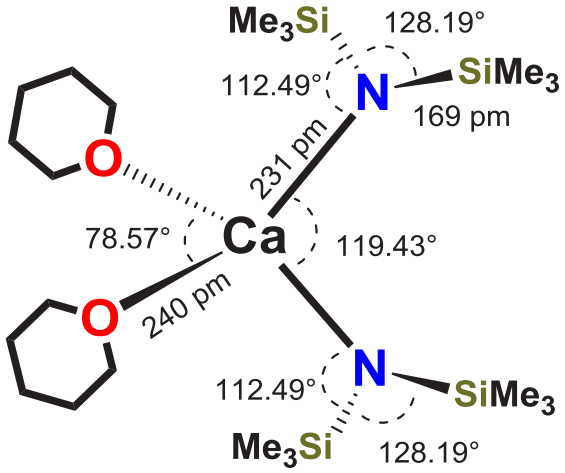


Figure 4.1: $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ ([**1**]).

A slight elongation of the Ca-N and Ca-O bonds in comparison to the thf adducts is observed because the smaller ether thf also represents the stronger base. This bond elongation allows to reduce the N-Ca-N bond angle in [**1**] in comparison to $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$, thus reducing the strain between the thp ligands and the amido anions.

The fact that homometallic calcium bis(amide) does not mediate hydroamination reactions raises the question of the cooperation of potassium and calcium in the catalyst system. This complex can be prepared by a two steps reaction. Metalation of 2,6-diisopropylaniline with $K[N(SiMe_3)_2]$ at higher temperature yields the corresponding potassium salt K{N(H)Dipp}. Then, the metathetical approach of the excess of this potassium salt with CaI_2 in THF leads to the formation of solvent-free calciate $[K_2Ca\{N(H)Dipp\}_4]_\infty$ [**2**].[162b]

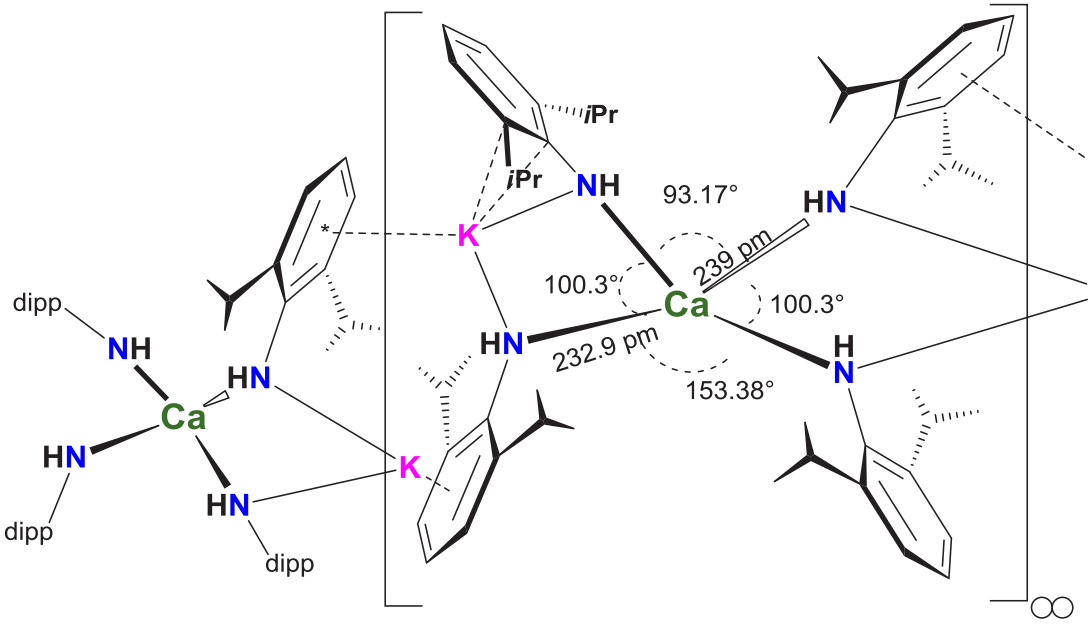
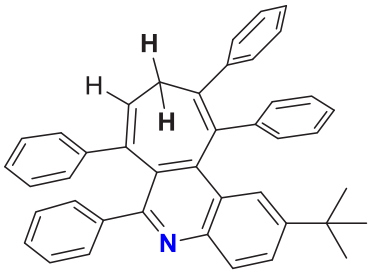


Figure 4.2: Section of the polymeric structure of [**2**].

In the solid state $K_2[Ca\{N(H)Dipp\}_4]$ forms a coordination polymer consisting of $[Ca\{N(H)Dipp\}_4]^{2-}$ anions interconnected by potassium cations. It can be assumed that in solution the calciate anions are maintained. In these calciate anions electrostatic repulsion between the amido substituents enhances the Ca-N bond lengths and, hence, nucleophilicity and reactivity of the amido groups. The role of the potassium ions remains unclear and speculative. Potassium ions are considered as soft Lewis acids being able to coordinate to

rather hard (such as ethers) and preferably to soft Lewis bases such as aromatics and extended π-systems. Nevertheless, it remains speculative in what extend this coordination behavior of K^+ supports the catalytic hydroamination via coordination to any of the reported intermediates. Special attention has to be turned to the advantageous properties of the catalyst system. The reaction of four equivalents of KN(H)Dipp with calcium iodide in THF yields solvent-free $K_2[Ca\{N(H)Dipp\}_4]$. The potassium ions bind to the amido anions and to the π-systems of the aryl groups leading to a coordination polymer in the solid state. Nevertheless, this complex is soluble in ethers. On one hand, the rather bulky isopropyl groups in *ortho*-position prevent the formation of ether adducts which commonly tend to slowly lose these neutral coligands upon standing and handling. Partial loss of coligands (desolvation) leads to weathering of the crystalline material and makes it difficult to exactly meet the stoichiometry. On the other hand, these isopropyl groups enhance intramolecular steric strain which can be released by a ligand exchange reaction and therefore, in solution, a fast substitution of the 2,6-diisopropylanilide anion by smaller amide or phosphide ligands occurs. This initial amide or phosphide exchange, which is much faster than the addition to the alkyne moieties, is the reason that $K_2[Ca\{N(H)Dipp\}_4]$ ([**2**]) represents an ideal precatalyst for any hydrofunctionalization of diphenylbutadiyne with sterically less demanding primary or secondary arylamines as well as diphenylphosphane. In addition, this calciate is soluble in ethereal solvents enabling the preparation of stock solutions. The crystalline compound as well as the stock solutions of this complex are stable and can be stored under anaerobic conditions.

Using of the catalyst [**2**] to mediate the addition of primary arylamines (**Figure 3.3**) across the diyne backbone under kinetic control (at room temperature) leads to the unique formation of unsaturated seven-membered rings, depending on the ortho substituents of the arylamines (**Figure 4.3** [**3**], [**4**], [**5**] and [**6**]). In contrast, the hydroamination of the same primary arylamines (**Figure 3.3, a, b, c, e,** and **f**) under thermodynamic control (in boiling THF) yields *N*-aryl-2,5-diphenylpyrroles regardless of the bulkiness of the *N*-bond aryl groups (**Figure 4.3**, [**7**], [**8**], [**9**], [**10**] and [**11**]).



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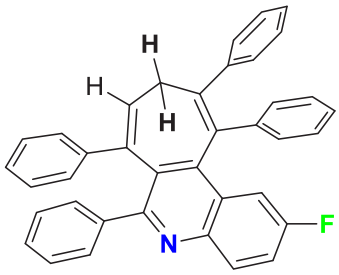

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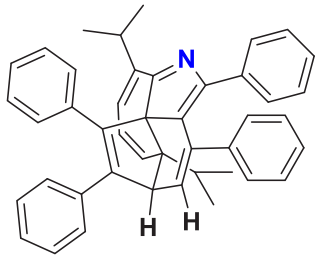

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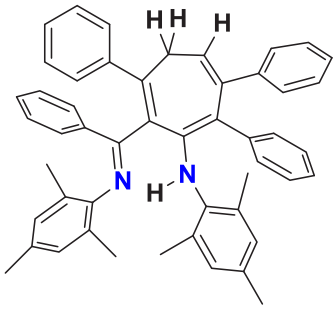

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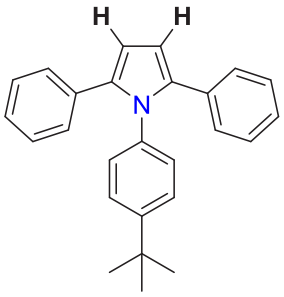

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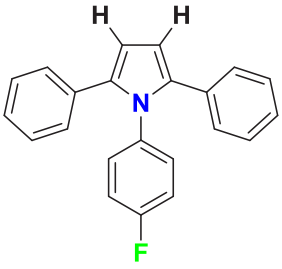

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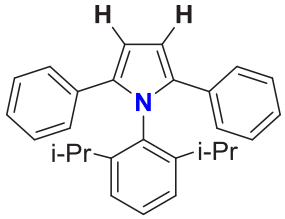

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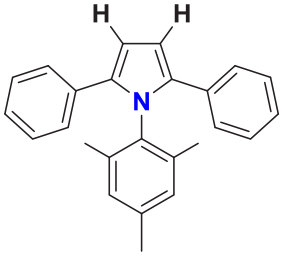

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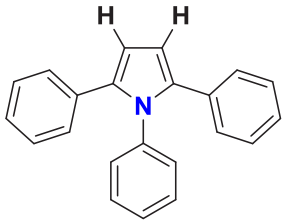


[11]

Figure 4.3: Hydroaminated diphenylbutadiyne by primary arylamines.

The precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ was also used to study the hydroamination of diphenylbutadiyne with secondary arylamines. Using of secondary arylamines lead us to the less complicated products. After approximately 6 h a nearly complete conversion with a catalyst loading of 5 mol-% yields singly hydroaminated butadiyne. Diverse para-substituents such as H, Me and F were tested and gave the desired hydroamination products (*N*-methyl)-(*N*-aryl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine of the type [Ph-C≡C-CH=C (Ph)]N(Me)(C_6H_4-4-R) with R = H [**12**], Me [**13**] and F [**14**]. This hydroamination was regioselective; however, both stereoisomers with *E*- and *Z*-arrangement at the C=C double bond were formed. The second calcium mediated hydroamination step of the other C≡C triple bond which has not been reported before, requires much longer time at similar reaction conditions. After three days mixtures of singly and doubly hydroaminated diphenylbutadiyne were obtained if *N*-methylaniline was employed and complete doubly hydroaminated diphenylbutadiyne was obtained if *N*-methyl-4-fluoroaniline was employed. In contrast to this finding, no significant amounts of doubly hydroaminated diphenylbutadiyne was observed in the NMR spectra for the hydroamination with *N*-methyl-4-tolylamine. Again, the catalytic hydroamination gave regioselectively 1,4-diphenyl-1,4-bis(*N*-methylanilino)buta-1,3-diene [**15**] and [**16**] but a mixture of *E,E*-, *E,Z*- and *Z,Z*-stereoisomers were obtained. The extremely decelerated second hydroamination allowed the isolation of pure singly hydroaminated diphenylbutadiyne. The catalytic hydroamination of [**12**] with *N*-methyl-4-fluoroaniline yielded exclusively the mixed doubly hydroaminated product [**17**] as a stereoisomeric mixture. The absence of [**15**] and [**16**] verifies that an amination-deamination equilibrium can be excluded.

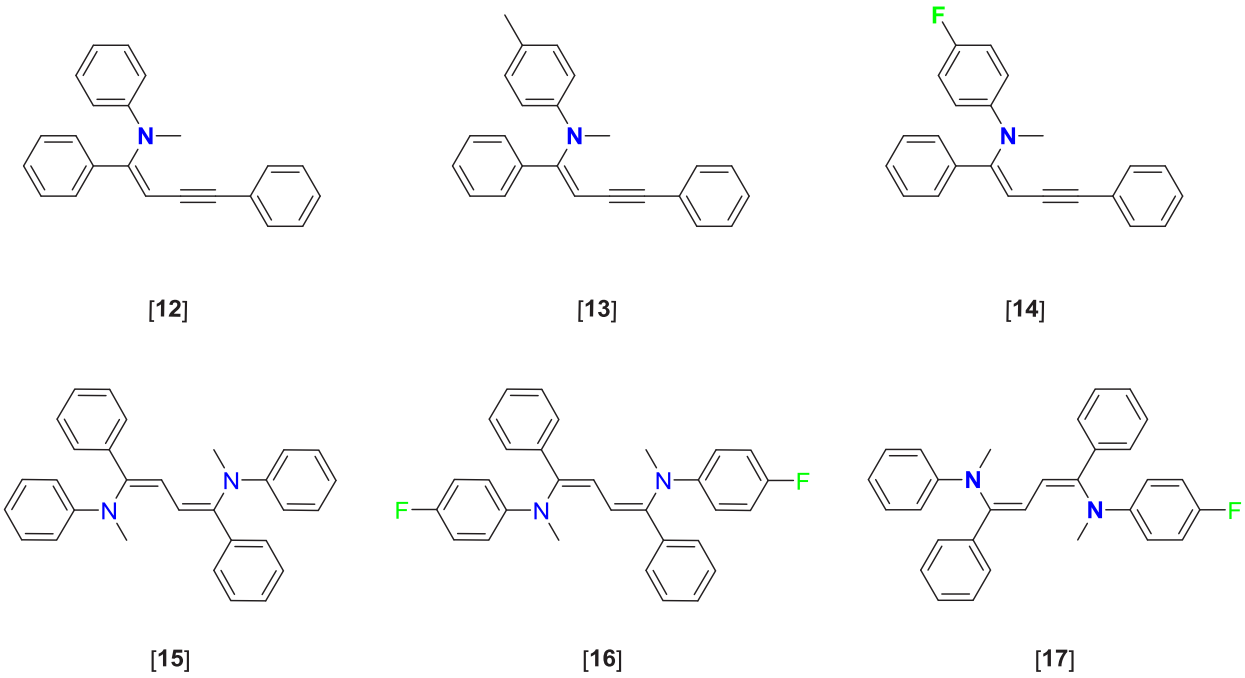


Figure 4.4: Products of singly and doubly hydroaminated diphenylbutadiyne by secondary arylamines.

The X-ray structures of *E*-isomeric [**12**], [**13**] and [**14**] suggest that the lone pair of the nitrogen atoms show only a very small interaction with the π-systems of the adjacent C=C double bonds whereas no delocalization into the *N*-bound aryl groups can be substantiated. The second amino group enhances steric strain and in *Z,Z*-isomeric [**15**], [**16**] and [**17**] the lone pairs of the nitrogen atoms slightly interact with the π-systems of the *N*-bound aryl groups. This observation suggests that steric reasons might account for the significantly slower second hydroamination step.

Moreover, the proven catalyst [**2**] was an effective catalyst not only for hydroamination reactions but also for hydrophosphanylation reactions, where the addition of diphenylphosphane across the C≡C triple bond of compounds [**12**], [**13**] and [*] ([*] is 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne) yields the compounds [**18**], [**19**] and [**20**] (**Figure 4.5**). Both hydropentelation steps are regioselective but only the catalytic addition of the H-P bond also stereoselectively yields the *E*- isomer as shown in **Figure 4.5**.

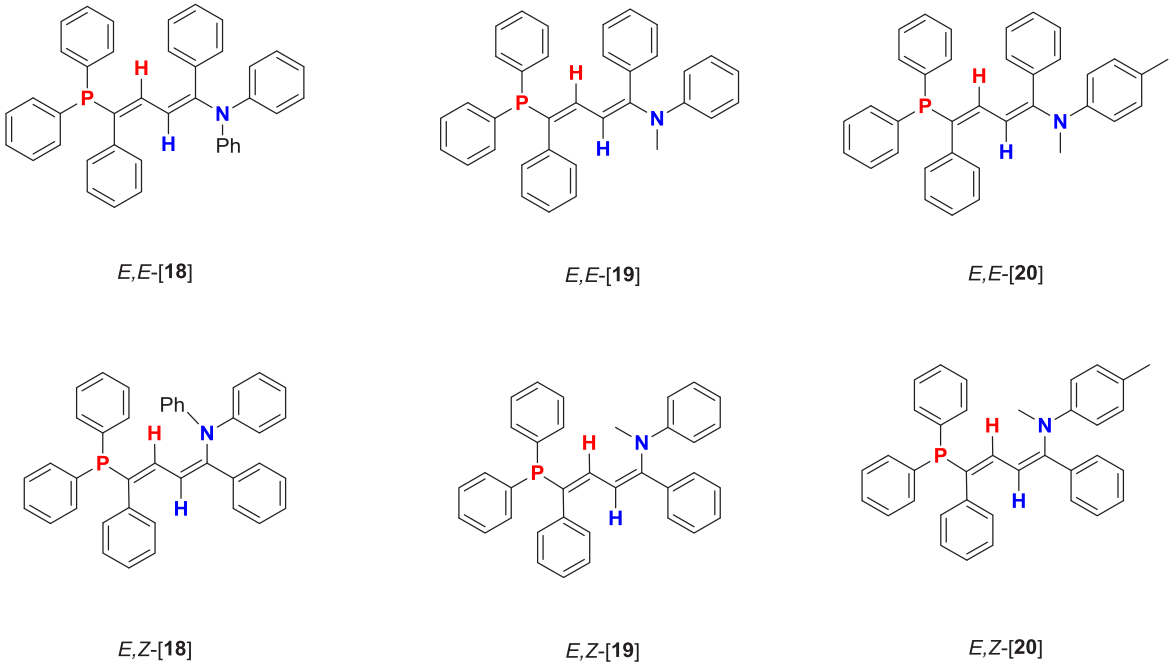
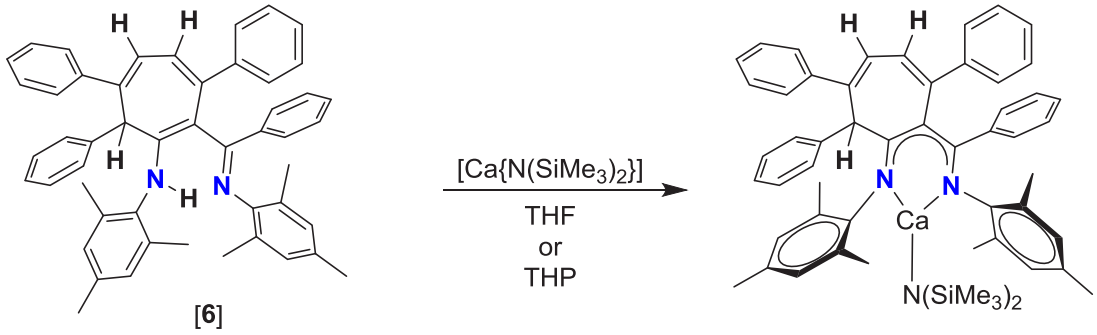


Figure 4.5: Products of hydropentelation of diphenylbutadiyne by secondary amines and phosphane.

In the near future the focusing point will be on the control of the stereo- and regio- selectivity of hydropentelation reactions. We assume that these objectives can be achieved via protection of the catalytic center by bulky groups. Hence, we will investigate compound [**6**] in the transamination reaction with [Ca{N(SiMe$_3$)$_2$}] (**Scheme 4.1**) because it contains the novel β-diketimine unit. Simple β-diketiminate complexes have already been successfully used to catalyze hydroamination and hydrophosphanylation reactions as mentioned in the introduction part.



Scheme 4.1: Proposed scheme for transamination of [(L)$_2$Ca{N(SiMe$_3$)$_2$}].

5 Zusammenfassung (Deutsche Version)

Aus der vorliegenden Arbeit geht hervor, dass Additionsreaktionen von diversen primären und sekundären Aminen (Hydroaminierung) sowie von Diphenylphosphan (Hydrophosphanylierung) an C≡C Dreifachbindungen von 1,4-Diphenylbutadiin auf effiziente Weise durch ein amid-basiertes Kalium-Calciat katalysiert werden können. Diese heterobimetallische Komplexverbindung steht in Konkurrenz zu etablierten Übergangsmetall- und Lanthanoid- basierten Katalysatoren, die in der Einleitung der Dissertation erwähnt werden. Es ist von Bedeutung, dass die hier untersuchten Hydroaminierungen und -phosphanylierungen regioselektiv stattfinden und die Hydrophosphanylierung zusätzlich eine Stereoselektivität aufweist. Zu Beginn dieser Arbeit lag der Fokus auf der Modifikation des Calcium-hexamethyldisilazids $[(L)_2Ca\{N(SiMe_3)_2\}_2]$ hinsichtlich der Koliganden L und einer daraus resultierenden potentiellen Nutzbarkeit für katalytische Anwendungen. Allerdings konnte letztere für L = thf und L = thp bezüglich einer Hydroaminierung nicht nachgewiesen werden. Das halogenfreies Addukt $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ ([**1**]) ist in einkristalliner Form über die Transmetallierung von Zinn(II)-*bis*[bis(trimethylsilyl)amid] mit metallischem Calcium und anschließender Umkristallisation aus *n*-Hexan leicht verfügbar. Diese farblose Komplexverbindung zeigt eine gute Löslichkeit in gängigen organischen Lösungsmitteln. Die Veränderung der strukturellen Eigenschaften des THP-Adduktes im Vergleich zum THF-Addukt wird durch den vergrößerten sterischen Anspruch des THP dominiert, was auch bei THP-Addukten von CaI_2 und Arylcalciumiodid beobachtet wurde.

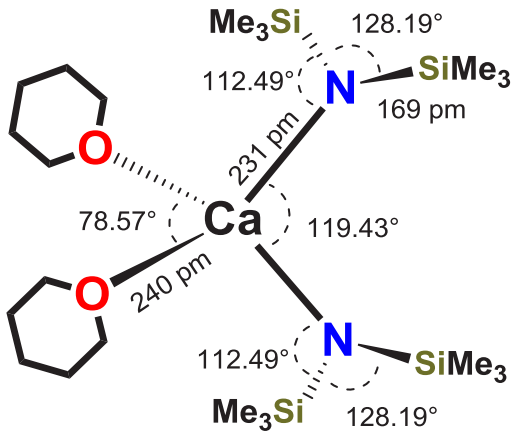


Abbildung 5.1: $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ ([1]).

Im Vergleich zu dem THF-Addukt wird eine leichte Verlängerung der Ca-O-Bindungen beobachtet, was mit der geringeren Nucleophilie des THP einhergeht. Der vergrößerte sterische Anspruch des THP veranlasst eine Verringerung des N-Ca-N-Bindungswinkels in [**1**] im Vergleich zu $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$, wodurch die Spannung zwischen den THP-Liganden und den Amid- Anionen reduziert wird.

Die Tatsache, dass das Calcium-bis(amid) Hydroaminierungsreaktionen nicht vermitteln konnte, wirft die Frage nach der Kooperation von Kalium und Calcium in dem hier verwendeten Katalysatorsystem [**2**] auf. Dieser Komplex kann durch eine zweistufige Reaktion hergestellt werden. Die Metallierung von 2,6-Diisopropylanilin mit $K[N(SiMe_3)_2]$ bei 100 °C ergibt das entsprechende Kaliumsalz K[N(H)DIPP], welches anschließend in einer Salzmetathese mit CaI_2 in THF zum lösungsmittelfreien Calciat $[K_2Ca\{N(H)DIPP\}_4]_\infty$ [**2**] umgesetzt wird.

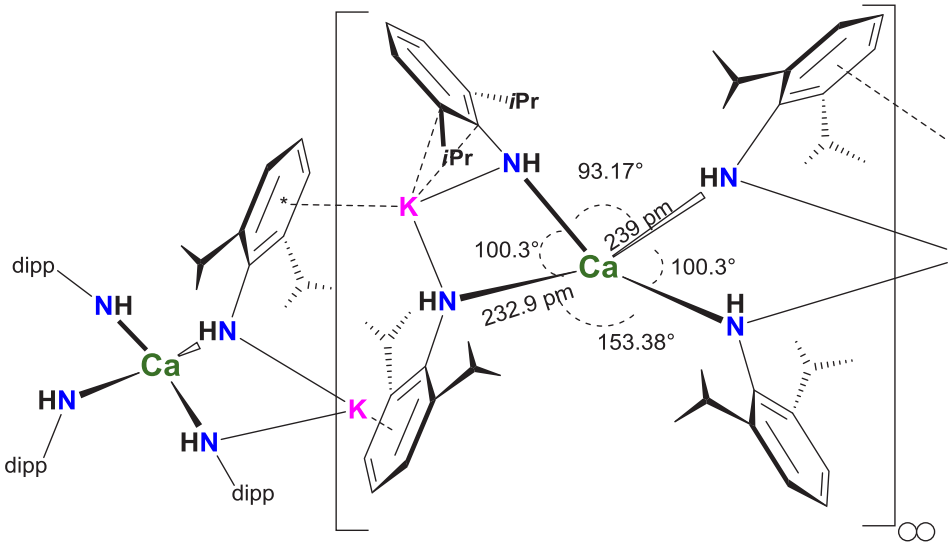


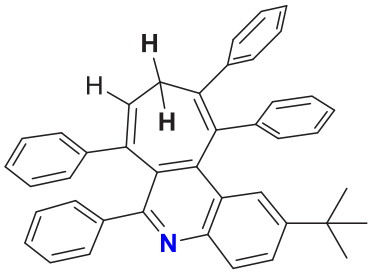
Abbildung 5.2*:* Ausschnitt der polymeren Struktur von [**2**].

Es wird angenommen, dass die Isopropyl-Gruppen in *ortho*-Position die Anlagerung von Ko-Liganden wie Ethermoleküle verhindern. Im kristallinen Zustand bildet $K_2[Ca\{N(H)Dipp\}_4]$ ein Koordinationspolymer, bestehend aus $[Ca\{N(H)Dipp\}_4]^{2-}$ Anionen, welche durch Kaliumkationen unter Ausbildung von K-π-Wechselwirkungen miteinander verbrückt werden. In diesen Calciat-Anionen, welche in Lösung erhalten bleiben, sind elektrostatische Abstoßungen zwischen den Amiden für eine Erhöhung der Ca-N-Bindungslängen und somit der Nucleophilie und Reaktivität verantwortlich. Über den

Anteil der Reaktivitätssteigerung durch die Kaliumionen kann bislang nur spekuliert werden. Kaliumionen sind als weiche Lewis-Säuren in der Lage, an harte (z.B Ether) sowie vorzugsweise an weiche Lewis-Basen, wie Aromaten und ausgedehnte π-Systeme zu koordinieren. Allerdings bleibt es bisher ungeklärt, was der Beitrag des Koordinationsverhaltens von K^+ z.B. zu der Stabilisierung eines Übergangszustandes in der Hydroaminierung ist.

Die Bildung der etherfreien Struktur im festen Zustand erleichtert die Handhabbarkeit, welche bei Ether-Addukten nicht gegeben ist, da die teilweise Freisetzung jener Koliganden zu Gewichtsverlust führen kann. Dies könnte eine genaue Einwaage und somit das Treffen der korrekten Stöchiometrie verhindern. Auf der anderen Seite erhöhen die Isopropylgruppen die intramolekulare sterische Spannung, was zu einer schnellen Substitution des 2,6-Diisopropylanilid- Anions durch kleinere Amid oder Phosphanid Liganden führt. Dieser anfängliche Amid oder Phosphanid-Austausch, welcher viel schneller als die Addition an die Alkin-Einheiten ist, ist der Grund dafür, dass K_2[Ca{N(H)DIPP}$_4$] ([**2**]) einen idealen Präkatalysator für die Hydrofunktionalisierung von Diphenylbutadiin mit sterisch weniger anspruchsvollen primären oder sekundären Arylaminen sowie Diphenylphosphan darstellt. Darüber hinaus ist dieses Calciat in etherischen Lösungsmitteln löslich, was die Herstellung von Stammlösungen ermöglicht. Die kristalline Verbindung sowie die Stammlösungen dieses Komplexes sind stabil und können unter anaeroben Bedingungen aufbewahrt werden.

Die Addition von primären, *ortho*- substituierten Arylaminen (**Figure 3.3**) an das Diin-Rückgrat unter Verwendung des Katalysators [**2**] führt unter kinetischer Kontrolle (bei Raumtemperatur) zu der spezifischen Bildung ungesättigter Siebenringe (**Abbildung 5.3** [**3**], [**4**], [**5**] und [**6**]). Im Gegensatz dazu führt die Hydroaminierung der gleichen primären Arylamine (**Figure 3.3**, **a**, **b**, **c**, **e**, und **f**) unter thermodynamischer Kontrolle (in siedendem THF) zu *N*-Aryl-2,5-diphenylpyrrolen unabhängig vom sterischen Anspruch der *N*-gebundenen Arylgruppen (**Abbildung 5.3**, [**7**], [**8**], [**9**], [**10**] und [**11**]).



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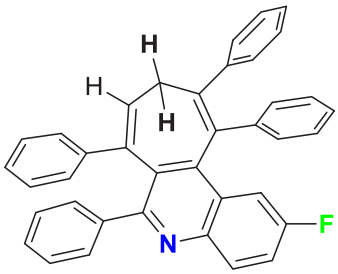

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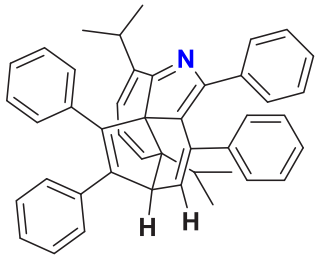

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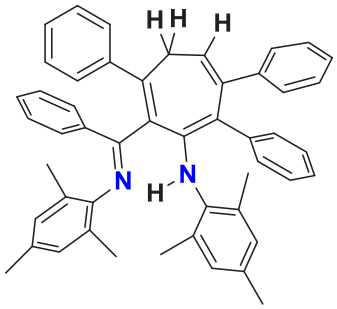
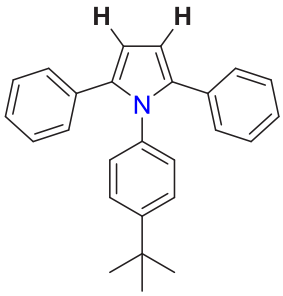


[6]



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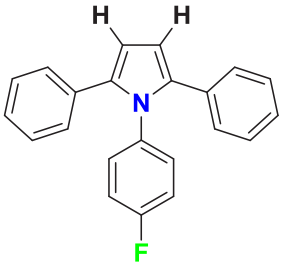

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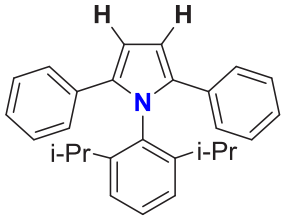

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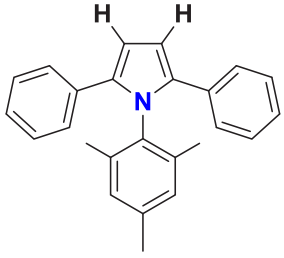

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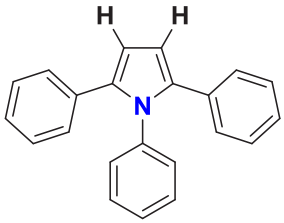
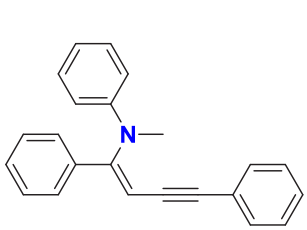


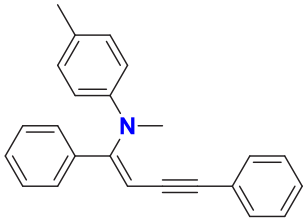
[11]

Abbildung 5.3: Mit prämieren Aminen hydroaminiertes Diphenylbutadiin.

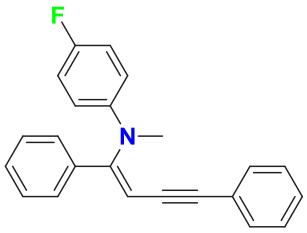
Der Präkatalysator $K_2[Ca\{N(H)DIPP\}_4]$ wurde außerdem zur Addition von sekundären *N*-Methyl- Anilinen an Diphenylbutadiin verwendet, woraufhin wesentlich unkompliziertere Produkte erhalten wurden. Bei einer Reaktionszeit von 6 h bei Raumtemperatur und einer Katalysatorbeladung von 5 mol-% kann ein nahezu vollständiger Umsatz zu einfach hydroaminierten Produkten beobachtet werden. Diverse *para*- substituierte Aniline (H, Me, F) führten mit sehr guten Ausbeuten zum vergleichbaren (*N*-methyl)-(*N*-aryl)-1,4-diphenylbut-1-en-3-in-1-ylaminen des Typs [Ph–C≡C–CH=C(Ph)]N(Me)(C_6H_4-4-R) mit R = H [**12**], Me [**13**] und F [**14**]. Diese Reaktionen verliefen regioselektiv, jedoch nicht stereoselektiv, was die Bildung von *E*- und *Z*- Isomeren mit sich bringt. Die Hydroaminierung der verbliebenen Dreifachbindung findet bei gleichen Bedingungen allerdings erst nach langen Reaktionszeiten statt, was als Resultat aus der Erhöhung des sterischen Drucks der zweiten Aminofunktion anzusehen ist. Nach drei Tagen konnte im Fall von *N*- Methylanilin ein Gemisch aus einfach und doppelt hydroaminierten Produkten ([**12**] und [**15**]) und im Fall von *N*-Methyl-4-fluoranilin ein vollständiger Umsatz zum 1,4-Diphenyl-1,4-bis(*N*-methyl-4-fluoranilino)buta-1,3-dien ([**16**]) festgestellt werden. Diese Produkte liegen allerdings als Gemisch aus *E,E*-, *E,Z*- und *Z,Z*- Isomeren vor. Im Fall von *N*-Methyl-4tolylanilin fand hingegen keine zweite Addition statt. Der extrem verzögerte zweite Additionsschritt ermöglicht es, das einfach hydroaminierte Produkt zu isolieren und nachträglich zu funktionalisieren. So konnte [**12**] mit *N*-Methyl-4-fluoranilin zum gemischt doppelt hydroaminierten [**17**] umgesetzt werden. Da das Reaktionsgemisch keine Spuren von [**15**] und [**16**] enthält, kann ein Aminierungs-Deaminierungs-Gleichgewicht ausgeschlossen werden.



[12]



[13]



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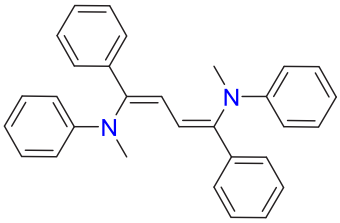
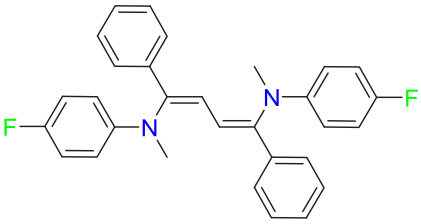


[15]



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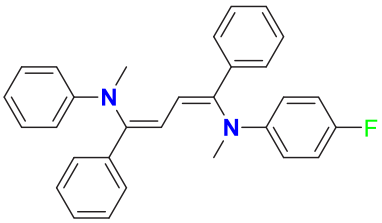
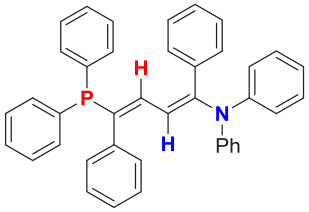


[17]

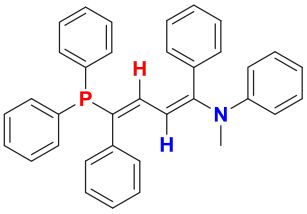
Abbildung 5.4*:* Produkte von einfach und doppelt hydroaminiertem Diphenylbutadiin durch sekundäre Arylamine.

Die Molekülstrukturen der *E*-Isomere von [**12**], [**13**] und [**14**] verdeutlichen, dass das freie Elektronenpaar am Stickstoffatom nur sehr schwach mit dem π-System der benachbarten C=C Doppelbindungen interagiert und keine Delokalisation in die *N*-gebundenen Arylgruppen stattfindet. In den doppelt hydroaminierten Produkten [**15**], [**16**] und [**17**] ist dies auch der Fall.

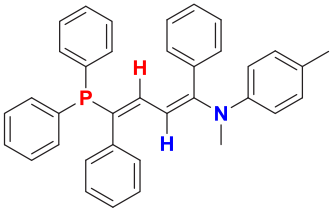
Abschließend konnte gezeigt werden, dass durch den Präkatalysator $K_2[Ca\{N(H)DIPP\}_4]$ auch Additionen von Diphenylphosphan an die (*N*-methyl)-(*N*-aryl)-1,4-diphenylbut-1-en-3-in-1-ylamine [**12**], [**13**] und [*] ([*] ist 1-Diphenylamino-1,4-diphenylbut-1-en-3-in-1-ylamine) katalysiert werden können. Dies ermöglichte die Isolierung der Verbindungen [**18**], [**19**] und [**20**], wobei die Hydrophosphanylierung regio- und stereoselektiv abläuft.



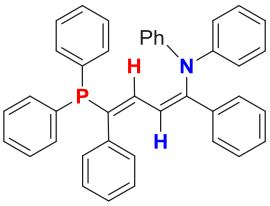
E,E-[**18**]



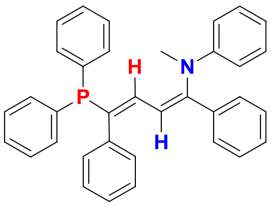
E,E-[**19**]



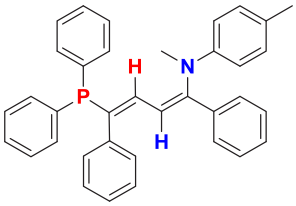
E,E-[**20**]



E,Z-[**18**]



E,Z-[**19**]



E,Z-[**20**]

Abbildung 5.5: Produkte der Hydropentelation von Diphenylbutadiin mit sekundären Aminen und Phosphan.

6 Experimental part

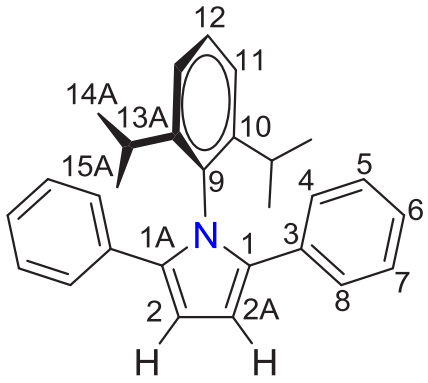
General remarks:

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. The solvents were dried over KOH and subsequently distilled over sodium/ benzophenone under a nitrogen atmosphere prior to use. Methanol was dried over magnesium pieces and methylene chloride over CaH_2 and stored over molecular sieve 3Å. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. ^{1}H, $^{13}C\{1H\}$, ^{31}P and ^{19}F NMR spectra were recorded on Bruker AC 200 AC 400 and AC 600 spectrometers. Chemical shifts are reported in parts per million relative to DDS (4,4-dimethyl-4-silapentane-1-sulfonic acid) for the ^{1}H and $^{13}C\{1H\}$ NMR measurements, D_3PO_4 (Phosphoric acid-d_3) for ^{31}P and $^{31}P\{1H\}$ NMR measurements and trifluorotoluene for ^{19}F NMR measurements as external standard. The residual signals of the deuterated solvents [D_8]THF, $CDCl_3$ and CD_2Cl_2 were used as internal standards. All substrates were purchased from *Sigma Aldrich*, *Merck* or *Alfa Aesar* and used after distillation, only diphenylbutadiyne has been used without further purification. Mass spectra were obtained on a Finnigan MAT SSQ 710. IR spectra were recorded on the Perkin Elmer FT-IR-Spectrometer System 2000 as *Nujol* mulls between KBr windows and on a ATR-IR spectrometer. Elemental analysis on a LECO CHNS-932 apparatus gave values for C, H, N, and S.

X-Ray structure determination. The intensity data for the compounds were collected on a *Nonius-Kappa-CCD* diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for *Lorentz* and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[187] The structures were solved by Direct Methods (SHELXS) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97).[188] The hydrogen atoms (with exception of methyl groups) were located by difference Fourier synthesis and refined isotopically. All non-hydrogen atoms were refined anisotropically.[188] Crystallographic data as well as structure solution and refinement details are already published.[162b, 164, 182, 184, 186] The program XP (*SIEMENS* Analytical X-ray Instruments, Inc.)[189] and POV-Ray were used for structure representations.[190]

6.1 Unpublished result

6.1.1 Synthesis of *N*-(2,6-diisoprpylphenyl)-2,5-diphenylpyrrole [**10**]



Diphenylbutadiyne (0.25 g 1.23 mmol) was dissolved in 17 mL of THF before 2,6 diisopropylaniline (0.219 g, 1.23 mmol) and 10 mol-% of the calciate $K_2[Ca\{N(H)Dipp\}_4]_\infty$ (5 mol-% at the beginning and 5 mol-% after 3 d) were added and the reaction mixture heated for 6 d at 60 °C. Thereafter, the solution was hydrolyzed with 15 mL of distilled water, extracted with diethyl ether and the separated ether phase dried with sodium sulfate. Recrystallization from pentane at 5 °C yielded a colorless solid (0.34 g, 0.89 mmol, 72.8 %) in an orange mother liquor. M.P. 165.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 -7.58 (m, 4H, Ar-*H*), 7.44 - 7.21 (m, 9H, Ar-*H*), 7.11 - 7.09 (s, 2H), 3.36 - 3.21 (hept. 2H, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.44 - 0.89 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.21 (*C*6), 145.82 (*C*1, *C*1A), 138.5, 134.8, 132.9, 132.9, 131.5, 130, 129.5, 129.1, 128.8, 128.3, 128, 127.6, 127.3, 126.7, 112.3, 111.6 (*C*2, *C*2A), 27.8 (*C*13, *C*13A), 25.87 (*C*14, *C*15, *C*14A, *C*15A). MS [EI, m/z (%)]: 378 (70) $[M]^+$, 379 (100) [M], 313(40), 260 (20), 191 (10), 77 (10) [Ph]. IR 3064 w, 3028 w, 2912 w, 1702 w, 1599 m, 1542 w, 1482 s, 1388 m, 1336 m, 1299 m, 1076 m, 1027 m, 862 s, 786 m, 761 s, 746 vs, 691 vs, 619 s, 603 m, 508 m.

6.2 Published results

Compound number	*Compound name*	*Literature*
[**1**]	Bis(tetrahydropyran)Calcium Bis[bis(trimethylsilyl)amide]	[164]
[**2**]	Dipotassium-tetrakis(diisoprobylanilido)calciate	[162b]
[**3**]	2-(*tert*-Butyl)-6,7,10,11-tetraphenyl-9*H*-cyclohepta[c]quinoline	[182]
[**4**]	2-(Fluoro)-6,7,10,11-tetraphenyl-9*H*-cyclohepta[c]quinoline	[182]
[**5**]	2,6-Diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.01,7.02,13]pentadeca-3,5,7,9,11,14-hexaene	[182]
[**6**]	*N*-Mesityl-7-(*E*)-((mesitylimino)(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine	[182]
[**7**]	*N*-(4-Tert-Butyl)phenyl)-2,5-diphenylpyrrole	[182]
[**8**]	*N*-(4-Fluorophenyl)-2,5-diphenylpyrrole	[182]
[**9**]	*N*-Mesityl-2,5-diphenylpyrrole	[182]
[**10**]	*N*-(2,6-Diisoprpylphenyl)-2,5-diphenylpyrrole	this work
[**11**]	*N*-Phenyl-2,5-diphenylpyrrole	[182]
[**12**]	1-(*N*-Methyl-anilino)-1,4-diphenylbut-1-ene-3- yne	[184]
[**13**]	1-(*N*-Methyl-para-toluidino)-1,4-diphenylbut-1-ene-3- yne	[184]
[**14**]	1-(*N*-Methyl-para-fluoroanilino)1,4-diphenylbut-1-ene-3-yne	[184]
[**15**]	1,4-di(*N*-Methyl-anilino)-1,4-diphenylbuta-1,3-diene	[184]
[**16**]	1,4-di(*N*-Methyl-4-fluoroanilino)buta-1,4-Diphenyl-1,3-diene	[184]
[**17**]	1-(*N*-Methyl-anilino)-4-(*N*-methyl-para-fluoroanilino) 1,4-diphenylbut-1,3-diene	[184]
[**18**]	1-(Diphenylphosphanyl)-1,4-diphenyl-4-(diphenylamino)buta-1,3-diene	[186]
[**19**]	1-(Diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-anilino)buta-1,3-diene	[186]
[**20**]	1-(Diphenylphosphanyl)-1,4-diphenyl-4-(*N*-methyl-tolylamino)-buta-1,3-diene	[186]

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8 Attachment

Attached publications

1. **Fadi M. Younis**, Helmar Görls, Sven Krieck, Matthias Westerhausen. Synthesis and structural characterization of bis(tetrahydropyran)calciumbis[bis(tri-methylsilyl)amide]. *Z. Anorg. Allg. Chem.* **2013**, 19-21
2. Carsten Glock, **Fadi M. Younis,** Steffen Ziemann, Helmar Görls, Wolfgang Imhof, Sven Krieck, Matthias Westerhausen. 2,6-Diisopropylphenylamides of Potassium and Calcium A Primary Amido Ligand in s-Block Metal Chemistry with an Astonishing Reactivity. *Organometallics* **2013**, 32, 2649-2660
3. **Fadi. M. Younis**, S. Krieck, H. Görls, M. Westerhausen. S-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines Using a Dipotassium Tetrakis(amino)calciate Precatalyst. *Organometallics* **2015***, 34,* 3577-3585.
4. **Fadi. M. Younis**, S. Krieck, H. Görls, M. Westerhausen. Hydroamination of diphenylbutadiyne with secondary *N*-methyl-anilines using the dipotassium tetrakis(2,6-diisopropylanilino)calciate precatalyst. *Dalton Trans*., **2016**, 45, 6241-6250.
5. **Fadi. M. Younis**, S. Krieck, T.M. A. Al-shboul, H. Görls, M. Westerhausen. Calcium-Mediated Catalytic Synthesis of 1-(Diorganylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes. *Inorg. Chem*. **2016**, 55, 4676-4682.

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Synthesis and Structural Characterization of Bis(tetrahydropyran)calcium Bis[bis(trimethylsilyl)amide]

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Keywords: Calcium; Amides; Transmetalation; Bis(trimethylsilyl)amide; Tetrahydropyran

Abstract. Transmetalation of $Sn[N(SiMe_3)_2]_2$ with calcium granules in tetrahydropyran (thp) yields colorless $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ (**1**) which is soluble in common organic solvents. The calcium center is in a distorted tetrahedral environment with Ca–N and Ca–O bond lengths of 231.08(11) and 240.23(9) pm, respectively. The molecular structure is dominated by steric factors leading to a NCaN bond angle of 119.43(6)°.

Introduction

The initial synthesis of the bis(trimethylsilyl)amides of the heavier alkaline earth metals by various methods approximately twenty years ago offered a valuable reagent for a fruitful organocalcium chemistry because these amides are soluble in common organic solvents.[1–4] The major access routes include salt-metathesis reactions of $KN(SiMe_3)_2$ with CaI_2,[5–7] transmetalation of $M[N(SiMe_3)_2]_2$ with Ca (M = Hg,[8] Sn[9]) and direct metalation of $HN(SiMe_3)_2$ with calcium in the presence of ammonia[10] or $BiPh_3$.[11] Recently, *Johns* et al.[12] showed that the salt-metathesis reactions can yield $Ca[N(SiMe_3)_2]_2$ that is contaminated with $KN(SiMe_3)_2$ and therefore they recommend metalation of the amine with dibenzylcalcium. The popularity of $Ca[N(SiMe_3)_2]_2$ in s-block metal chemistry is based on easy preparative procedures, solubility in common organic solvents, non-toxicity of the metals, tunability of the reactivity by various methods such as variation of the bulkiness of substituents or the base strength of the solvent. In addition, the conversion to alkali metal tris(amido) calciates[13–15] or calcium metalates (e.g. zincates[16]) represent concepts to alter the reactivity of these amides.[17]

The calcium–nitrogen bonds in calcium bis(amides) show a highly ionic nature and the bonding situation is dominated by electrostatic attraction between the cation and the anions as well as repulsive forces between anions. Thus, the bulkiness of the ligands plays a prominent role with respect to the coordination number of calcium. In addition, Ca^{2+} represents a Lewis acid forming adducts with Lewis bases. Thus a coordination number of three requires bulky bases as, for example, in tris[bis(trimethylsilyl)amido]calciates.[13–15]

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Results and Discussion

Due to the tremendous importance of $Ca[N(SiMe_3)_2]_2$ in organocalcium chemistry many base adducts were prepared and structurally characterized. The tetrahydrofuran complex is the favored synthon for this chemistry, however, this ether exhibits ring strain and therefore ether cleavage can occur quite easily during metal-organic transformations. Therefore, we investigated the tetrahydropyran adduct of $Ca[N(SiMe_3)_2]_2$. In order to obtain halide-free $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ (**1**) we have chosen the transmetalation of freshly distilled $Sn[N(SiMe_3)_2]_2$ with calcium granules according to Equation (1). During this heterogeneous reaction the color of the solution turned reddish brown. After filtration the solvent was removed in vacuo and the residue recrystallized from *n*-hexane yielding pure **1**.

(1)

The molecular structure and the numbering scheme are displayed in Figure 1. The tetra-coordinate metal atom is in a severely distorted tetrahedral coordination sphere with a large N1–Ca1–N1A angle of 119.4°. The nitrogen atoms are in distorted trigonal planar environments with an average N–Si bond of 168.9 pm. This short bond is characteristic for bis(trimethylsilyl)amides bound at electropositive s-block metals[18] because the hyperconjugation of negative charge from the p_z(N) orbital into σ*(Si–C) orbitals strengthens the N–Si bonds. The bulkiness of the trimethylsilyl groups enforces a large Si1–N1–Si2 bond angle.

In order to evaluate structural characteristics, mononuclear calcium bis[bis(silyl)amides] are summarized in Table 1. The compounds are arranged according to the coordination number of the calcium atom [CN (Ca)] and within these groups according to the Ca–N distances. It is obvious that bulkier silyl substituents lead to elongated Ca–N bonds which vary between 227 and 239 pm. The Ca–L distances (the donor atoms are

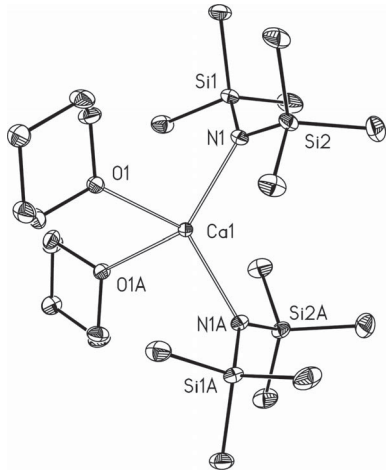

Figure 1. Molecular structure and numbering scheme of $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ (**1**). The ellipsoids represent a probability of 40%, hydrogen atoms are neglected for clarity reasons. Symmetry-related atoms (–*x*+1, *y*, –*z*+0.5) are marked with the letter "A". Selected bond lengths /pm: Ca1–N1 231.1(1), Ca1–O1 240.2(1), N1–Si1 168.8(1), N1–Si2 169.0(1), Ca1···C6 318.2(2), Ca1···Si1 346.6(1), Ca1···Si2 334.4(1); angles /deg: N1–Ca1–N1A 119.4(1), N1–Ca1–O1 94.3(1), N1–Ca1–O1A 134.9(1), O1–Ca1–O1A 78.6(1), Ca1–N1–Si1 119.3(1), Ca1–N1–Si2 112.5(1), Si1–N1–Si2 128.2(1).

given in brackets) strongly depend on the donor base because the atomic radii decrease from C over N to O. However, the major influence of these co-ligands on the Ca–N bond lengths seems to be of steric nature. Even the coordination number of calcium plays a minor role as can be seen from the complexes with three- and five-coordinate alkaline earth metal centers showing Ca–N values well within the range for adducts with tetra-coordinate calcium atoms. Free coordination sites can be shielded by agostic bonds to the trialkylsilyl groups as observed for $[(thf)_2Ca\{N(SiMe_3)(SiPh_3)\}_2]$.[20] A detailed discussion on such secondary bonds was provided by *Ruhlandt-Senge* and co-workers[4] (see also Ref. [26]). In **1**, rather short contacts of the calcium atom to trimethylsilyl groups additionally shield the metal atom.

In general, the N–Ca–N bond angles are large due to steric repulsion between the bulky bis(silyl)amido ligands and due to electrostatic repulsion between the anions. The smallest value is observed for $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ (**1**) because tetrahydropyran is a rather demanding cyclic ether. Larger co-ligands enhance the intramolecular steric strain whereas longer Ca–L bonds lead to strain relaxation. In comparison to the thf adduct $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$, the weaker base thp leads to longer Ca–O bonds. However, the bulkier ether thp also leads to a slight elongation of the Ca–N bonds and to a rather small N–Ca–N angle. Often complexes containing this cyclic ether ligands exhibit advantageous crystallization behavior in comparison to thf adducts because thf ligands tend to show large thermal motion and disordering in the solid state.[27,28]

Conclusions

The halide-free tetrahydropyran adduct $[(thp)_2Ca\{N(SiMe_3)_2\}_2]$ (**1**) is easily available in single-crystalline form via transmetalation of tin(II) bis[bis(trimethylsilyl)amide] and subsequent recrystallization from alkanes. This colorless complex shows good solubility in common organic solvents. The molecular structure is dominated by steric factors as also observed for adducts of CaI_2 and arylcalcium iodides.[27] A slight elongation of the Ca–N and Ca–O bonds in comparison to the thf adducts is observed because the smaller ether thf also represents the stronger base. This bond elongation allows to reduce the N–Ca–N angle in **1** in comparison to $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$[22] thus reducing the strain between the thp ligands and the amido anions. Due to the fact that thp is a weaker and bulkier base than thf, a slightly enhanced reactivity of **1** might be expected in comparison to $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$. In addition, substitution of the rather floppy thf by thp ligands, which adopt the chair conformation in the solid state, often improves the crystallization behavior

Table 1. Comparison of selected structural parameters of mononuclear calcium bis[bis(silyl)amides] of the type $[(L)Ca\{N(SiR_3)_2\}_2]$ [average values, bond lengths /pm and angles /°, CN(Ca) coordination number of calcium; dme 1,2-dimethoxyethane, thf tetrahydrofuran, thp tetrahydropyran, *t*BuIm *N*-tert-butylimidazole, tmeda tetramethylethylenediamine, py pyridine, dmap 4-dimethylaminopyridine, hmpa hexamethylphosphoric acid triamide).

L	$NSiR_3$	CN(Ca)	Ca–N /pm	Ca–L /pm	N–Ca–N /°	Ref.
NHC-1	$N(SiMe_3)_2$	3	229.0	259.8 (C)	125.4	[19]
NHC-2	$N(SiMe_3)_2$	3	230.3	262.9 (C)	124.5	[19]
thf	$N(SiMe_3)(SiPh_2tBu)$	3	232.3	238.2 (O)	134.6	[20]
dme	$N(SiMe_3)_2$	4	227.1	239.7 (O)	123.6	[21]
2 thf	$N(SiMe_3)_2$	4	230.2	237.7 (O)	121.3	[22]
2 thp	$N(SiMe_3)_2$	4	231.2	240.2 (O)	119.4	This work
1 tmeda	$N(SiMe_3)_2$	4	231.5	259.2 (N)	121.8	[23]
2 *t*BuIm	$N(SiMe_3)_2$	4	232.5	246.4 (N)	123.3	[24]
2 Ph_3PO	$N(SiMe_3)_2$	4	233.7	226.5 (O)	129.4	[19]
2 py	$N(SiMe_3)(SiMe_2tBu)$	4	235.3	253.7 (N)	125.3	[20]
2 thf	$N(SiMe_3)(SiPh_3)$	4	236.0	237.3 (O)	146.6[a]	[20]
2 dmap	$N(SiMe_3)(SiMe_2tBu)$	4	236.7	249.8 (N)	122.3	[20]
2 hmpa	$N(SiMe_3)(SiMe_2tBu)$	4	239.0	228.0 (O)	125.2	[20]
3 thf	$N(SiMe_2CH_2)_2$	5	233.6	240.2 (O)	136.8[b]	[25]

a) Coordination number 4+2 due to two additional agostic interactions to trimethylsilyl groups; b) trigonal bipyramidal environment of calcium with the amido ligands in equatorial positions.

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of metal complexes thus facilitating the isolation of crystalline and pure material.

Experimental Section

Synthesis: All procedures and manipulations of the compounds were performed in an anhydrous nitrogen atmosphere. The synthesis was performed in analogy to a literature procedure.[9] The NMR spectra were recorded at room temp. at [D_6]benzene solutions. Calcium granules (0.5 g, 12.5 mmol) and 5,4 g (12,5 mmol) of tin(II) bis[bis(trimethylsilyl)amide] were combined in THP (50 mL). After a few hours the solution turned dark red. After 9 h stirring at room temperature the reaction was finished and the color of the reaction mixture was reddish brown. Afterwards, the reaction mixture was filtered. The solvent of the filtrate was removed in vacuo and the residue recrystallized from *n*-hexane. At –5 C°, 3.8 g of colorless crystals (7,1 mmol, 56,8 %) precipitated that were suitable for X-ray diffraction studies. *Physical data*: M.p.: 149 °C. **^{1}H NMR:** δ = 0.37 (s, 18 H, $SiMe_3$), 1.13 (m, 2 H, thp, *p*-CH_2), 1.20 (m, 4 H, thp, *m*-CH_2), 3.59 (m, 4 H, thp, *o*-CH_2). **^{13}C{^{1}H} NMR:** δ = 5.85 ($SiMe_3$), 22.46 (thp, *p*-CH_2), 25.95 (thp, *m*-CH_2), 70.44 (thp, *o*-CH_2). MS (EI): 161 (20 %), 147 (50 %), 146 (100 %), 130 (70 %), 86 (12 %, $[thp]^+$). **IR** (Nujol, KBr windows): 1457 vs, 1377 s, 1310 w, 1251 vs, 1178 m, 1092 w, 1077 w, 1047 s, 967 w, 931 s, 883 sh, 842 s, 748 m, 683 w, 662 m, 606 w, 590 m, 571 m cm^{-1}. Elemental analysis was impossible because the mass of the substance was not constant during weighing and handling due to loss of ligand once isolated.

Structure Determination: The intensity data for the compounds was collected with a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data was corrected for Lorentz and polarization effects but not for absorption effects.[29,30] The structures were solved by direct methods (SHELXS[31]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[31]). The hydrogen atoms were located by difference Fourier synthesis and refined isotropically.[31] All non-hydrogen atoms were refined anisotropically.[29] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. *Crystal Data for* **1**: $C_{22}H_{56}CaN_2O_2Si_4$, 533.13 g·mol^{-1}, colorless prism, size 0.06 × 0.06 × 0.04 mm^3, monoclinic, space group *C*2/*c*, a = 17.9171(3), b = 11.0021(2), c = 17.7543(4) Å, β = 107.312(1)°, V = 3341.28(11) $Å^3$, T = –140 °C, Z = 4, $\rho_{calcd.}$ = 1.060 g·cm^{-3}, μ(Mo-K_α) = 3.5 cm^{-1}, F(000) = 1176, 10106 reflections in h(–22/23), k(–14/11), l(–23/23), measured in the range 3.51° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 99.7 %, 3829 independent reflections, R_{int} = 0.0243, 3431 reflections with $F_o > 4\sigma(F_o)$, 253 parameters, 0 restraints, $R1_{obs}$ = 0.0309, $wR2_{obs}$ = 0.0737, $R1_{all}$ = 0.0361, $wR2_{all}$ = 0.0773, GOOF = 1.070, largest difference peak and hole: 0.281/–0.183 e·$Å^{-3}$.

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-903644 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

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2,6-Diisopropylphenylamides of Potassium and Calcium: A Primary Amido Ligand in s-Block Metal Chemistry with an Unprecedented Catalytic Reactivity

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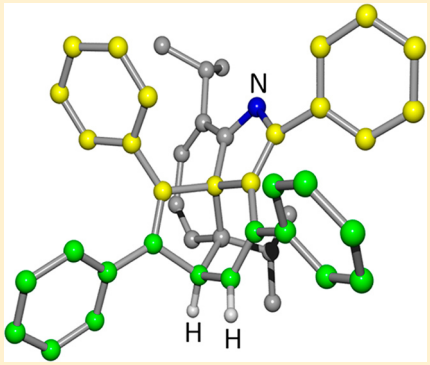
Supporting Information

ABSTRACT: Transamination of $KN(SiMe_3)_2$ with 2,6-diisopropylphenylamine (2,6-diisopropylaniline) in toluene at ambient temperature yields $[K\{N(H)Dipp\}\cdot KN(SiMe_3)_2]$ (**1**) regardless of the applied stoichiometry. Recrystallization of **1** in the presence of tetramethylethylenediamine (TMEDA) and tetrahydrofuran (THF) leads to the formation of $[(\mu\text{-thf})K_2\{N(H)Dipp\}_2]_\infty$ (**2**), whereas potassium bis(trimethylsilyl)amide remains in solution. Addition of pentamethyldiethylenetriamine (PMDETA) gives $[(pmdeta)K\{N(H)Dipp\}]_2$ (**3**). In contrast to the thf and pmdeta adducts, which lead to dissociation of **1** into homoleptic species, addition of bidentate dimethoxyethane maintains the mixed complex $[(dme)K\{\mu\text{-}N(SiMe_3)_2\}\{\mu\text{-}N(H)Dipp\}K]_2$ (**4**). A complete transamination of 2,6-diisopropylaniline with $KN(SiMe_3)_2$ in toluene at 100 °C yields $[K\{N(H)Dipp\}]$ (**5**), which reacts with CaI_2 to give $[(thf)_nCa\{N(H)Dipp\}_2]$ (**6**), $[(pmdeta)Ca\{N(H)Dipp\}_2]$ (**7**), and $[(dme)_2Ca\{N(H)Dipp\}_2]$ (**8**), depending on the solvents and coligands. Excess potassium 2,6-diisopropylphenylamide allows the formation of the calciate $[K_2Ca\{N(H)Dipp\}_4]_\infty$ (**9**). Hydroamination of diphenylbutadiyne with 2,6-diisopropylaniline in the presence of catalytic amounts of **9** gives tetracyclic 2,6-diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.0^{1,7}.0^{2,13}]pentadeca-3,5,7,9,11,14-hexaene (**10**). Solid-state structures are reported for **2**−**4** and **7**−**10**. Compound **10** slowly rearranges to tetracyclic 5a,9-diisopropyl-2,3,10,11-tetraphenyl-5a,6-dihydro-2a^1,6-ethenocyclohepta[*cd*]isoindole (**11**), which is slightly favored according to quantum chemical studies.



INTRODUCTION

Substituted amides of the electropositive s-block metals represent valuable reagents for diverse applications such as metalation, transamination, and amide transfer. Whereas several reviews exist discussing structures, properties, and reactivity of alkali-metal amides,[1] interest in organyl-substituted alkaline-earth-metal bis(amides) has been limited mainly to magnesium derivatives for a long time.[2] The homologous heavier alkaline-earth-metal complexes have attracted attention only for about the last two decades.[3,4] Early attempts gave insoluble, poorly characterized, and partially pyrophoric alkaline-earth-metal amides.[5] Approximately 20 years ago, the breakthrough succeeded with the synthesis of the alkaline-earth-metal bis[bis(trialkylsilyl)amides], which are soluble in common organic solvents such as ethers and aromatic and aliphatic hydrocarbons, allowing homogeneous reaction conditions.[6]

In recent years the portfolio of amides of the heavy alkaline-earth metals Ae became versatile. Solubility was guaranteed by substitution of only one trialkylsilyl group of $Ae\{N(SiMe_3)_2\}_2$ by an aryl substituent, leading to substituted trimethylsilylanilides.[3,7] Recently also diphenylamides[8] and *N*-alkylanilides[9] have been prepared and structurally characterized. In contrast to these complexes, which are soluble in tetrahydrofuran (THF), the 2,2,6,6-tetramethylpiperidylcalcium complexes express an enormous reactivity and cannot be handled in THF because of ether degradation processes.[9] In contrast to the case for stable amidomagnesium halides these Hauser-type bases of calcium show ligand redistribution processes (Schlenk-type equilibrium) favoring homoleptic calcium bis(amide) and calcium dihalide.[10]

Primary anilides of the heavier alkaline-earth metals tend to form aggregates (Ca) or even polymers (Sr, Ba) in the solid state and are only sparingly soluble in Lewis basic donor solvents.[11] 2,6-Difluoroanilides form more soluble complexes, but fluorine substituents in metal organic compounds may be hazardous and decompose spontaneously and violently.[12] *o*-Alkyl-substituted anilides form monomeric complexes with a strongly Lewis basic coligand such as hexamethylphosphoric acid triamide (hmpa), and mononuclear complexes of the type $[(hmpa)_3Ae\{N(H)Dipp\}_2]$ (Dipp = C_6H_3-2,6-iPr$_2$) were isolated.[3]

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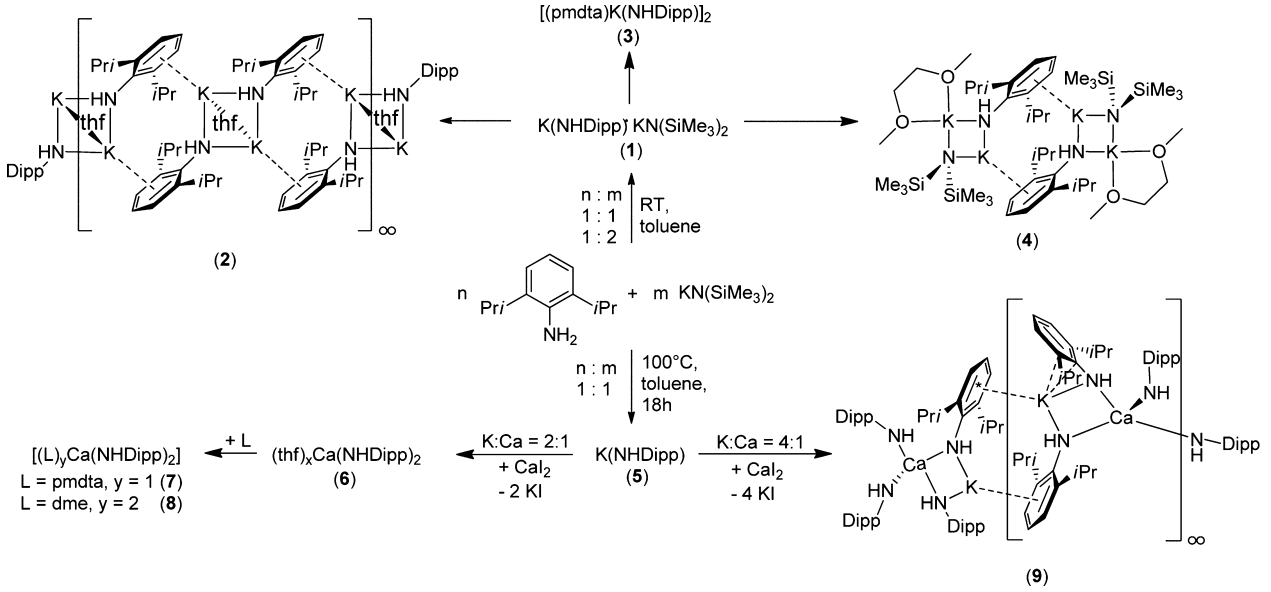
Scheme 1. Reaction Scheme for the Synthesis of Potassium, Calcium, and Mixed-Metal 2,6-Diisopropylanilides



Heterobimetallic s-block metal amides exhibit significantly enhanced reactivity. Mixed alkali-metal−magnesium amides tend to form inverse crowns which react as highly reactive metalation reagents,[13] whereas the alkali-metal−calcium derivatives can best be described as alkali-metal calciates due to the amido transfer from the alkali metal to calcium.[9,14−16]

The awakened interest in these alkaline-earth-metal amides is also based on the catalytic activity (for recent general reviews see ref 17) in hydroamination reactions of carbodiimides,[18] alkenes,[19,20] and alkynes.[16,20] Especially calcium is a very attractive inexpensive element, due to its worldwide availability and nontoxicity regardless of the concentration. In many catalytic applications Ae$\{N(SiMe_3)_2\}_2$ was employed as the precatalyst, intermediately forming the catalytically active calcium amides. We could demonstrate that often highly reactive heterobimetallic compounds such as potassium calciates are required to catalyze the addition of amines to carbon−carbon multiple bonds.[16]

RESULTS AND DISCUSSION

Synthesis. Transamination of $KN(SiMe_3)_2$ with 2,6-diisopropylphenylamine (H_2N-Dipp) in toluene at room temperature led to precipitation of $[K\{N(H)Dipp\}\cdot KN(SiMe_3)_2]$ (**1**) regardless of the applied stoichiometry. The formation of a solid precipitate impeded the complete conversion to potassium 2,6-diisopropylphenylamide. Addition of Lewis bases often yields smaller and soluble aggregates which allow spectroscopic characterization. Compound **1** was dissolved in a mixture of tetramethylethylenediamine (TMEDA) and tetrahydrofuran (THF), and from this solution crystals of $[(\mu\text{-thf})K_2\{N(H)Dipp\}_2]_\infty$ (**2**) precipitated, whereas potassium bis(trimethylsilyl)amide remained in solution (Scheme 1). A similar finding was observed upon addition of a solvent mixture of pentamethyldiethylenetriamine (PMDETA) and THF, yielding crystalline $[(pmdeta)K\{N(H)Dipp\}]_2$ (**3**), whereas $KN(SiMe_3)_2$ remained in the mother liquor. In contrast to the thf and pmdeta adducts, which led to dissociation of **1** into homoleptic species, addition of bidentate 1,2-dimethoxyethane (DME) maintained the mixed stoichiometry and tetranuclear $[(dme)K\{\mu\text{-}N(SiMe_3)_2\}\{\mu\text{-}N(H)Dipp\}\text{-}K]_2$ (**4**) was isolated.

More drastic reaction conditions during transamination of $KN(SiMe_3)_2$ with H_2N-Dipp gave solvent-free $K\{N(H)Dipp\}$ (**5**), which was used as an amide transfer reagent. The metathesis reaction of this potassium amide with calcium diiodide yielded the oily substance $[(thf)_nCa\{N(H)Dipp\}_2]$ (**6**) in solvents such as THF, hexane, toluene, and mixtures thereof. The addition of tridentate pmdeta or bidentate dme led to crystalline $[(pmdeta)Ca\{N(H)Dipp\}_2]$ (**7**) and $[(dme)_2Ca\{N(H)Dipp\}_2]$ (**8**), respectively. Excess potassium 2,6-diisopropylphenylamide yielded the calciate $[K_2Ca\{N(H)Dipp\}_4]_\infty$ (**9**), which precipitated from a THF solution as a solvent-free coordination polymer.

The influence of the metals on the chemical ^1H and $^{13}C\{^1H\}$ NMR shifts of the 2,6-diisopropylphenylamide ions is small and seems to be not especially diagnostic of structure. Therefore, a detailed discussion is not included and the data are given in the Supporting Information. 2,6-Diisopropylaniline shows low-field-shifted ^1H NMR resonances of the aryl and amino hydrogen atoms. For the potassium derivatives these signals are high-field-shifted; however, the values of the calcium complexes are very similar. The tertiary CH fragments of the isopropyl groups show chemical shifts of δ 3.15 and 3.00 for the potassium and calcium anilides, respectively.

In the $^{13}C\{^1H\}$ NMR spectra the largest differences are observed for the ipso-carbon atoms; deprotonation of 2,6-diisopropylaniline leads to a significant low-field shift. The formation of heterobimetallic potassium tetrakis(anilido)-calciate shifts the resonance of the ipso-carbon back toward a higher field. The influences of the metal and the environment of the amido functionality (terminal or bridging position) on the other carbon atoms are very small, and no dependency is observed for the chemical shifts of the isopropyl groups.

On the basis of NMR parameters structure elucidation is impossible. All s-block metal amides **1**−**9** show only one set of resonances with very similar chemical shifts. This finding is in agreement with the expectation that in ionic amides the nature of the metal atoms plays an ancillary role. Dissociation of these complexes and fast dynamic behavior on the NMR time scale

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(thus breaking up polymeric structures) explain not only this observation but also solubility in common organic donor solvents. Due to the fact that information on solution structures is very limited, we investigated the solid-state structures in order to verify the formation of homometallic and mixed s-block metal amides and to study the influence of coordinated solvent molecules.

Molecular Structures. Schematic representations are given in Scheme 1, and the molecular structures of the potassium amides **2**–**4**, and the calcium bis(anilides) **7** and **8** as well as the coordination polymer **9** are discussed in detail.

The molecular structure and numbering scheme of a section of polymeric **2** are shown in Figure 1. The central structural

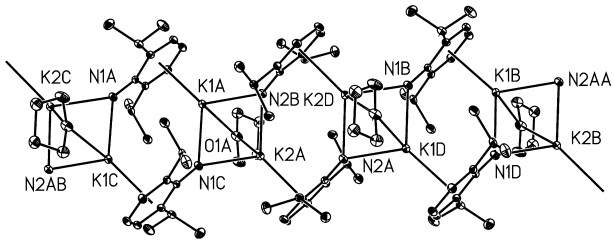

Figure 1. Section of polymeric **2**. The ellipsoids represent a probability of 40%, and H atoms are neglected for clarity. Symmetry-related atoms are marked with the letters A–D. Selected bond lengths (pm): K1A–N1C = 277.9(2), K1A–N2B = 275.4(2), K1A–O1A = 294.7(2), K2A–N1C = 277.3(2), K2A–N2B = 275.2(2), K2A–O1A = 286.8(2), K1A–C1A = 318.2(2), K1A–C2A = 316.7(2), K1A–C3A = 314.8(2), K1A–C4A= 313.3(2), K1A–C5A = 313.3(2), K1A–C6A = 317.3(2), K2A–C13A = 315.0(2), K2A–C14A = 322.0(2), K2A–C15A = 320.9(2), K2A–C16A = 314.4(2), K2A–C17A = 306.8(2), K2A–C18A = 306.6(2), N1C–C1C = 135.6(2), N2B–C13B = 135.8(2).

fragment consists of a four-membered K_2N_2 ring (average K–N distance 276.4 pm) with a bridging thf ligand between the potassium atoms. Thus, there exist three bridges between the alkali-metal atoms, leading to a short K1···K2 contact of only 349.1(1) pm. The dinuclear units are aligned to a one-dimensional strand via Lewis acid–base interactions between the soft potassium cations and the π systems of neighboring anilide moieties.

Enhancing the denticity and base strength of the neutral coligand allows the isolation of molecular dinuclear potassium anilides. The molecular structure and numbering scheme of **3** are displayed in Figure 2. The central structural fragment is the centrosymmetric planar four-membered K_2N_2 ring with different K–N bond lengths of 279.4(3) and 291.6(3) pm. The shorter K–N distance belongs to an interaction between K1 and an sp^2 hybrid orbital of N1, whereas the other potassium shows a more side-on coordination to the anilide anion (p_z orbital at N1), leading also to rather short contacts to C1 (314.8(3) pm) and C6 (329.3(3) pm). The nonbonding trans-annular K1···K1A contact adopts a rather large value of 421.1(1) pm. The coordination sphere of potassium is saturated by nitrogen bases of the pmdeta ligand, which shows two short K–N bonds (289.2(3) and 296.9(3) pm) and one significantly larger K–N distance of 318.3(3) pm.

The central four-membered K_2N_2 ring is also formed for heteroleptic $[(dme)K\{\mu\text{-}N(SiMe_3)_2\}\{\mu\text{-}N(H)Dipp\}K]_2$ (**4**), which is shown in Figure 3. The bulky bridging bis(trimethylsilyl)amide anions together with bidentate 1,2-dimethoxyethane hinder the formation of a one-dimensional

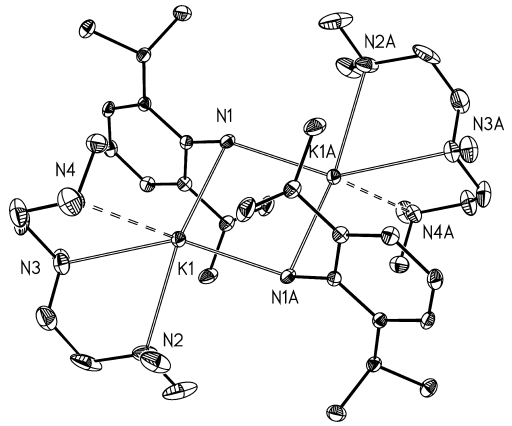

Figure 2. Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 40%, and H atoms are omitted for clarity. The symmetry-equivalent half of the molecule ($-x + 2$, $-y$, $-z + 1$) is marked with the letter A. Selected bond lengths (pm): K1–N1 = 291.6(3), K1–N1A = 279.4(3), K1–N2 = 289.2(3), K1–N3 = 296.9(3), K1–N4 = 318.3(3), N1–C1 = 136.3(4).

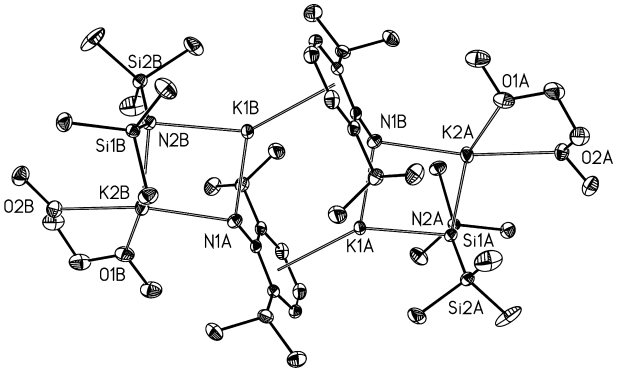

Figure 3. Molecular structure and numbering scheme of **4**. The ellipsoids represent a probability of 40%, and H atoms are neglected. The symmetry-related molecule halves ($-x + 2$, $-y + 1$, $-z$) are distinguished by the letters A and B. Selected bond lengths (pm): K1A–N1B = 274.2(1), K1A–N2A = 280.9(1), K2A–N1B = 276.3(1), K2A–N2A = 274.3(1), K2A–O1A = 273.3(1), K2A–O2A = 276.2(1), K1A–C1A = 320.3(1), K1A–C2A = 326.2(1), K1A–C3A = 323.5(2), K1A–C4A = 318.9(2), K1A–C5A = 315.3(2), K1A–C6A = 316.1(1), N1A–C1A = 135.9(2), N2A–Si1A = 166.8(1), N2A–Si2A = 166.8(1).

coordination polymer. Instead, two dinuclear units are interconnected by contacts between the potassium atoms and the π systems of the aryl groups. The highly ionic nature of the K–N interactions leads to strong electrostatic attractions between the nitrogen atom and the silicon atoms and, hence, short Si–N2 bonds of 166.8(1) pm due to back-donation of charge from the nitrogen atom to the silyl groups (hyperconjugation into σ^*(Si–C) bonds). The short N2–Si bonds enforce a large Si1–N2–Si2 bond angle of 133.43(8)° due to repulsive forces between the bulky trimethylsilyl groups. A similar effect was already discussed for dimeric $[KN(SiMe_3)_2]_2$.[21]

Crystalline monomeric 2,6-diisopropylanilides of calcium were obtained with multidentate coligands such as pmdeta and dme, yielding [(pmdeta)Ca{N(H)Dipp}$_2$] (**7**) and [(dme)$_2$Ca{N(H)Dipp}$_2$] (**8**), respectively. The molecular structure and numbering scheme of **7** is displayed in Figure 4. The pentacoordinate calcium atom binds to two anilide anions

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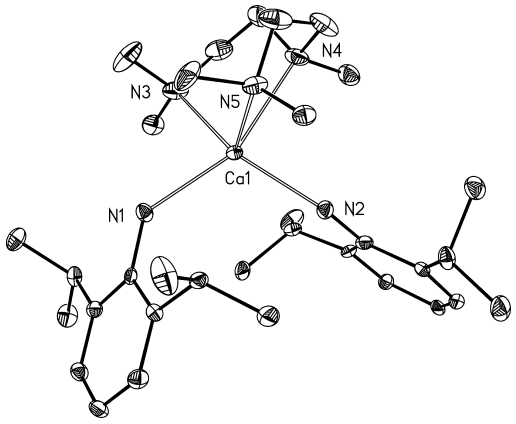

Figure 4. Molecular structure and numbering scheme of **7**. The ellipsoids represent a probability of 40%, and H atoms are not drawn. Selected bond lengths (pm): Ca1−N1 = 232.4(4), Ca1−N2 = 229.2(5), Ca1−N3 = 259.5(5), Ca1−N4 = 258.0(5), Ca1−N5 = 255.2(5), N1−C1 = 137.5(6), N2−C13 = 137.0(6). Selected bond angles (deg): N1−Ca1−N2 = 112.9(2), Ca1−N1−C1 = 136.7(3), Ca1−N2−C13 = 146.1(4).

and a tridentate pmdeta ligand. Due to additional electrostatic attraction the Ca1−N1 and Ca1−N2 distances to the anilides are more than 20 pm smaller than those to the pmdeta base. In addition, the small bite of the nitrogen bases of the pmdeta ligand (N···N distances) leads to very small N3−Ca1−N4 and N4−Ca1−N5 bond angles of 70.4(2) and 72.3(2)°. A rather small N1−Ca1−N2 bond angle of 112.9(2)° is enabled because the Ca1−N−C angles of the anilide ligands are widened to 136.7(3)° for N1 and 146.1(4)° for N2.

The complex $[(dme)_2Ca\{N(H)Dipp\}_2]$ (**8**) crystallizes in the centrosymmetric triclinic space group with four molecules A−D in the asymmetric unit. The molecular structure and numbering scheme of molecule A is represented in Figure 5. The hexacoordinate calcium atom is located in a significantly distorted octahedral environment due to small bites of the dme ligands and widened N−Ca−N angles. The larger coordination number of 6 leads to lengthened Ca−N bonds in comparison

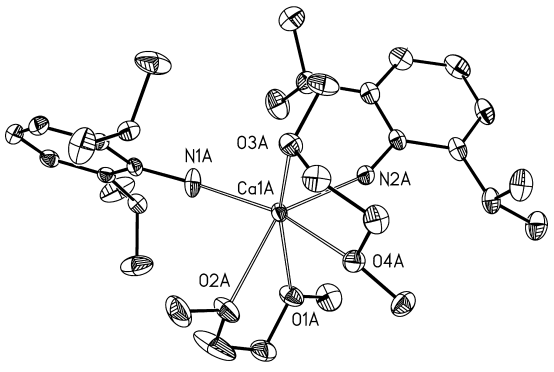

Figure 5. Molecular structure and numbering scheme of **8**. The ellipsoids represent a probability of 40%, and H atoms are omitted for clarity reasons. The asymmetric unit contains four molecules A−D; only molecule A is depicted. Selected bond lengths (pm): Ca1A−N1A = 230.6(4), Ca1A−N2A = 231.6(4), Ca1A−O1A = 242.5(3), Ca1A−O2A = 249.6(4), Ca1A−O3A = 242.8(3), Ca1A−O4A = 249.7(3), N1A−C1A = 136.9(5), N2A−C13A = 138.0(5). Selected bond angles (deg): N1A−Ca1A−N2A = 115.2(2), Ca1A−N1A−C1A = 156.8(3), Ca1A−N2A−C13A = 157.0(3).

to complex **7**. The N−Ca−N angles for the molecules A−D vary significantly and are larger for A, B, and D despite a larger coordination number (molecule A, 115.2(2)°; molecule B, 117.6(1)°; molecule C, 88.6(1)°; molecule D, 122.3(1)°), whereas molecule C deviates from the other molecules and a very small value is observed. Intramolecular strain leads to strongly widened Ca−N−C angles, and the four molecules show different values (molecule A, 156.8(3) and 157.0(3)°; molecule B, 137.0(3) and 154,6(3)°; molecule C, 147.5(3) and 149.6(3)°; molecule D, 159.2(3) and 137.4(3)°). The flexibility of the Ca−N−C angles supports the chemical intuition that electrostatic and steric forces dominate the structure and that covalent Ca−N bond contributions play insignificant roles.

In heterobimetallic amides the less electropositive metal commonly binds to the amido ligands, forming a metalate, whereas the more electropositive metal represents the countercation. We included the heterobimetallic amide with a potassium to calcium ratio of 2:1 in our structural investigations because mixed-metal amides often behave differently than the homometallic congeners.[13,14] The K to Ca ratio of 2:1 justifies considering this derivative as a higher order calciate. Therefore, the structure of the calciate $[K_2Ca\{N(H)Dipp\}_4]_\infty$ (**9**) was determined and a section of the coordination polymer is displayed in Figure 6. The calcium atom is in a distorted-

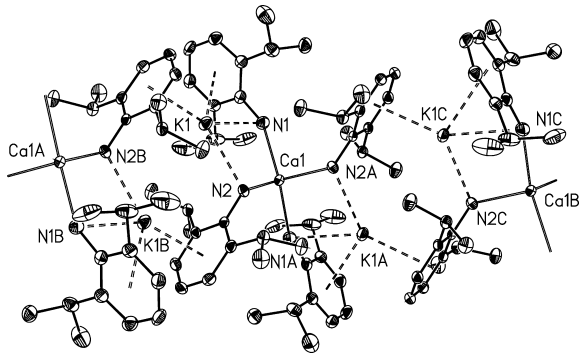

Figure 6. Section of the polymeric structure of **9**. The ellipsoids represent a probability of 40%, and H atoms are neglected for clarity . The letters A (−*x*, *y*, −*z* + 0.5) and B (−*x*, −*y* + 2, −*z*) characterize symmetry-related atoms. Selected bond lengths (pm): Ca1−N1 = 232.9(3), Ca1−N2 = 239.3(3), K1−N1 = 294.1(3), K1−C1 = 292.9(3), K1−N2 = 287.2(3), K1−C13B = 335.0(3), K1−C14B = 324.1(3), K1−C15B = 308.8(3), K1−C16B = 304.2(4), K1−C17B = 312.1(3), K1−C18B = 327.4(3), N1−C1 = 137.9(4), N2−C13 = 137.9(4). Selected bond angles (deg): N1−Ca1−N2 = 100.3(1), N1−Ca1−N1A = 152.4(2), N1−Ca1−N2A = 98.6(1), N2−Ca1−N2A = 93.2(1), Ca1−N1−C1 = 155.8(3), Ca1−N1−K1 = 90.5(1), Ca1−N2−C13 = 127.0(2), Ca1−N2−K1 = 90.93(9).

tetrahedral environment with N−Ca−N angles between 93.2(1) and 153.4(2)°. Despite the small coordination number of 4, rather large Ca−N bond lengths of 232.9(3) and 239.3(3) pm are observed due to electrostatic repulsion between the amide anions and intramolecular steric strain between the bulky aryl groups of neighboring amido ligands. The flexibility of the Ca−N−C bond angles (155.8(3) and 127.0(2)°) again supports the mainly ionic nature of this compound. These tetrakis(anilido)calciates are interconnected by potassium countercations that bind to the nitrogen atoms (K−N = 287.2(3) and 294.1(3) pm) and saturate their coordination sphere by Lewis acid−base interactions to the π systems of the aryl groups. The remarkable reactivity can be understood on

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Table 1. Average Bond Lengths (pm) of Selected Amides of Potassium and Calcium as Well as Their Mixed-Metal Derivatives[a]

compd	av Ca−N	av K−N	av Ca−L	av K−L	ref
		Potassium Amides			
$[KN(SiMe_3)_2]_2$		278.7			21
$[(tmeda)KTmp]_2$		279.2		295.1 (N)	22
$[(thf)_3KNPh_2]_2$		282.6		272.0 (O)	23
$[(pmdeta)KNPh_2]_2$		282.9		292.2 (N)	24
$[(pmdeta)KN(iPr)Ph]_2$		289.1		297.7 (N)	24
$[(dme)_2KN(iPr)Ph]_2$		287.3		286.8 (O)	24
$[(pmdeta)KN(H)Dipp]_2$		285.5		301.5 (N)	this work
$[(diox)_{1.5}KNPh_2]_\infty$		284.6		270.7 (O)	25
$[(tmeda)_{1.5}KNPh_2]_\infty$		287.4		290.5 (N)	26
$[\{KN(Me)Ph\}_3]_\infty$		282.4			24
$[\{(thf)_{0.5}KN(iPr)Ph\}_2]_\infty$		279.7		276.3 (O)	24
$[\{(thf)KN(iPr)Ph\}_5]_\infty$		280.8		272.9 (O)	24
$[(dme)_{0.25}KN(iPr)Ph]_\infty$		281.0		278.1 (O)	24
$[(thf)KN(H)Dipp]_\infty$		276.4		290.7 (O)	this work
		Calcium Amides			
$[(thf)_2Ca\{N(SiMe_3)_2\}_2]$	230.2		237.7 (O)		27
$[(dme)Ca\{N(SiMe_3)_2\}_2]$	227.1		239.7 (O)		28
$[(tmeda)Ca\{N(SiMe_3)_2\}_2]$	231.5		259.2 (N)		10
$[(tmeda)Ca(Tmp)_2]$	227.5		264.5 (N)		9
$[(tmeda)Ca\{N(iPr)_2\}_2]$	227.2		260.2 (N)		10
$[(dme)_2Ca(NPh_2)_2]$	236.9		246.1 (O)		8
$[(thf)_4Ca\{N(Me)Ph\}_2]$	241.5		240.7 (O)		12
$[(thf)_3Ca\{N(iPr)Ph\}_2]$	234.9		242.7 (O)		9
$[(thf)_2Ca\{N(SiMe_3)Dipp\}_2]$	232.6		235.6 (O)		7c
$[(thf)_2Ca\{N(SiMe_3)Mes\}_2]$	230.4		234.3 (O)		7b
$[(tmeda)Ca\{N(SiMe_3)Mes\}_2]$	231.1		252.9 (N)		7b
$[(dme)_2Ca\{N(H)Dipp\}_2]$	231.1		246.2 (O)		this work
$[(pmdeta)Ca\{N(H)Dipp\}_2]$	230.8		257.6 (N)		this work
		Potassium Calciates			
$[(thf)_4K_2Ca\{N(iPr)Ph\}_4]$	241.8			268.7	9
$[(tmeda)_2K_2Ca\{N(iPr)Ph\}_4]$	244.1	294.6		283.7	15
$[(thf)_3K_2Ca(NPh_2)_4]_\infty$	240.3			265.2	9
$[K_2Ca\{N(H)Dipp\}_4]_\infty$	236.1	290.7			Tthis work

[a]Abbreviations: diox, 1,4-dioxane; Dipp, 2,6-diisopropylphenyl; dme, 1,2-dimethoxyethane; L, neutral Lewis base such as ethers and amines; Me, methyl; Mes, 2,4,6-trimethylphenyl; Ph, phenyl; pmdeta, pentamethyldiethylenetriamine; Pr, propyl; thf, tetrahydrofuran; tmeda, tetramethylethylenediamine; Tmp, 2,2,6,6-tetramethylpiperidide.

the basis of a small coordination number of calcium (accessibility of calcium by the substrate) and of electrostatic repulsion between the anilide anions (enhancing the nucleophilicity and availability of the anilide anions) in addition to increased nucleophilicity caused by the electron-donating isopropyl groups.

Selected structural parameters of potassium and calcium amides are compared in Table 1. The amides of the heavier alkali metals and alkaline-earth metals have attracted tremendous interest because they react as highly reactive nucleophiles and metalation reagents as well as hydroamination catalysts.[17] The reactivity can be adjusted with the s-block metals potassium and calcium or even by employing their heterobimetallic derivatives. Due to a larger size of the potassium ion and its smaller charge, the Ca−N bonds are generally significantly shorter than the K−N bonds. Small variations depend on the coordination number of the s-block metals and on the bulkiness of the amides and coligands. In solvent-depleted compounds, the potassium ions also form strong bonds to the π systems of aryl groups, whereas solvent-free calcium amides dimerize via bridging amido ligands.[28] This π-philicity of the potassium ion was already investigated in detail at benzyl alkali-metal solvates;[29] whereas lithium and sodium ions show the shortest distances to the methylene unit, the potassium ion prefers a side-on coordination to the aromatic π system of the phenyl group. This finding supports the notion that the potassium ion represents a significantly softer cation than the lighter congeners and the doubly charged calcium ions. In heterobimetallic amides of potassium and calcium, the amido anions always bind to the harder divalent calcium ion, forming tetrakis(amido)calciates with tetracoordinate calcium centers. Due to the concentration of negative charge in the vicinity of calcium, neutral Lewis bases such as thf and tmeda bind at potassium. If the neutral coligands have weak coordination properties toward K^+ ions in comparison to the π systems of the phenyl groups, interactions between the potassium ion and the π systems of aryl substituents are operative, often leading to aggregation and formation of coordination polymers.

Hydroamination of Diphenylbutadiyne. Hydroamination is an atom-economic process for the preparation of substituted amines. However, thermodynamic and kinetic challenges aggravate the direct nucleophilic attack of the amine at an electron-rich C−C multiple bond. In addition, the large energy difference between the N−H and the C−C

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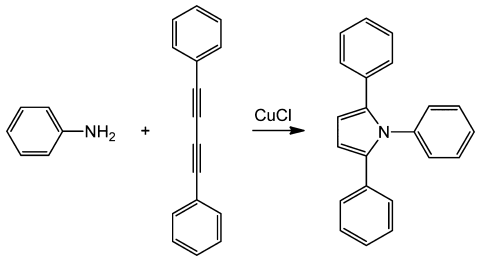
multiple bond and entropic effects are disadvantageous. Therefore, activation of the C−C multiple bond (by side-on coordination to transition metals) or of the amine (amide or imide formation at electropositive metals and lanthanoids) is required.

Intermolecular hydroamination of diphenylbutadiyne with diphenylamine required a very reactive catalyst.[16,20] Whereas the reactivity of the diphenylamides of potassium and calcium were insufficient to mediate this hydroamination reaction, catalytic amounts of heterobimetallic $[K_2Ca(NPh_2)_4]$ led to the formation of singly hydroaminated diphenylbutadiyne.[16] In contrast to this finding, the more nucleophilic *N*-isopropylanilides of potassium and of calcium are able to mediate the hydroamination of diphenylbutadiyne with *N*-isopropylaniline. The potassium-mediated hydroamination of diphenylbutadiyne with *N*-isopropylaniline gave small amounts of the side product 1-isopropylphenylamino-2,4-bis(phenylethynyl)-3-phenylnaphthalene with a 2:1 stoichiometry of diphenylbutadiyne to aniline.[16]

Hydroamination of butadiynes yielding pyrroles succeeds via a copper(I)-catalyzed addition of aniline to diphenylbutadiyne (Scheme 2).[30] Another strategy for the synthesis of pyrroles

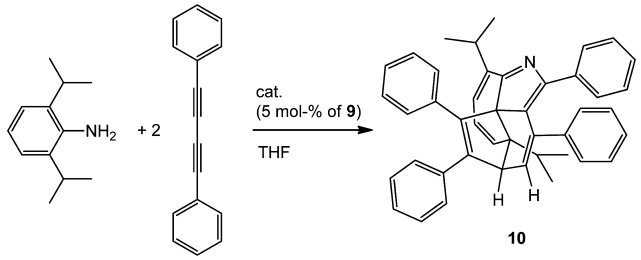
Scheme 2. Copper(I)-Mediated Synthesis of Pyrroles via Double Hydroamination of Diphenylbutadiyne with Aniline



was developed via the titanium-mediated double hydroamination of 1,4-pentadiynes with primary amines.[31] If benzylamine was used in these catalytic hydroamination reactions, pyridine derivatives were obtained.[30−32] Here we investigated the calcium-mediated hydroamination of diphenylbutadiyne with 2,6-diisopropylaniline. A single hydroamination would yield 1,4-diphenyl-1-(2,6-diisopropylanilino)-but-1-ene-3-yne, and a second intramolecular hydroamination step could allow the isolation of *N*-2,6-diisopropylphenylpyrrole. However, the hydroamination of diphenylbutadiyne with primary 2,6-diisopropylaniline proceeded surprisingly different in the presence of catalytic amounts of **9**. Similarly to the observation of the formation of the naphthalene side product,[16] 1 equiv of aniline reacted with 2 equiv of butadiyne, as shown in Scheme 3, regardless of the applied stoichiometry. In Figure 7 the color code clarifies the origin of the building blocks (black and blue, C and N of 2,6-diisopropylaniline; yellow and green, two diphenylbutadiyne units). This compound cocrystallized with half a diphenylbutadiyne molecule.

The resulting crystalline tetracyclic imine, 2,6-diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.0^{1,7}.0^{2,13}]-pentadeca-3,5,7,9,11,14-hexaene (**10**), was obtained with a yield of 82%. The formation of this product does not depend on the reaction temperature and succeeded in boiling THF and at ambient temperature; only the reaction period was extended at lower temperatures.

Scheme 3. Calciate-Mediated Hydroamination of Diphenylbutadiyne with 2,6-Diisopropylaniline in Tetrahydrofuran, Yielding Tetracyclic Imine 10[a]



[a]See text and Figure 7.

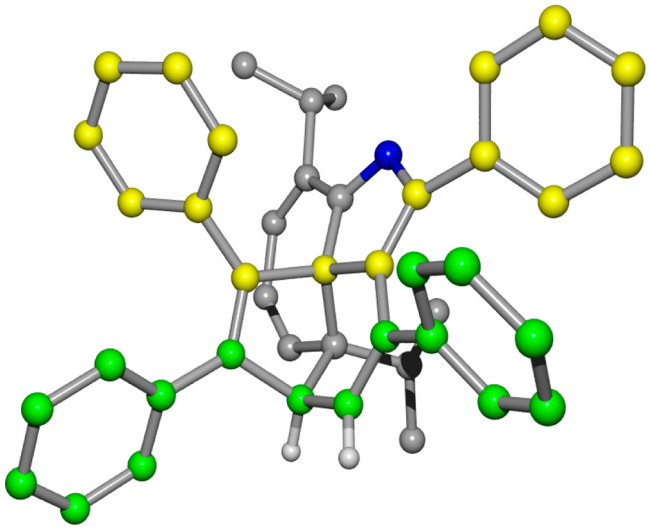


Figure 7. Ball-and-stick model of 2,6-diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.0^{1,7}.0^{2,13}]pentadeca-3,5,7,9,11,14-hexaene (**10**), clarifying the building blocks of this tetracyclic compound (black and blue, C and N of 2,6-diisopropylaniline; yellow and green, two diphenylbutadiyne units). The H atoms (light gray) are neglected, with the exception of those stemming from the aniline.

The molecular structure of **10** is displayed in Figure 8. The labeling of the atoms shows the numbering in accordance with the chemical name for the inner tetracyclic unit, with the nitrogen atom N8 being in position 8. For the numbering of the substituents, the digit of the adjacent ring atom was expanded by an additional digit to distinguish the carbon atoms within a substituent.

The nitrogen atom N8 is bound in a five-membered ring with a C7═N8 double bond and a N8−C9 single bond of 131.2(2) and 141.8(2) pm, respectively. From these values it is obvious that there is no significant delocalization within the conjugated system. A vast steric strain is introduced at the C1 atom, which is a member of all four cycles. This fact leads to severe deviations from a tetrahedral environment (C−C1−C values deviate from 101.2(1) to 120.3(2)°) toward a trigonal-pyramidal environment[33] and to a significant elongation of the C1−C bonds. The adjacent C2 atom even shows stronger deviations from ideal tetrahedral symmetry. The smallest C1−C2−C13 angle shows a value of only 95.7(1)° between three sp^3-hybridized carbon atoms and a C2−C13 bond length of 157.5(2) pm. Distortions also widen the angles at the vicinal diphenylethene fragment with C15−C14−C141 and C14−C15−C151 values of 129.9(2) and 130.1(2)°, respectively.

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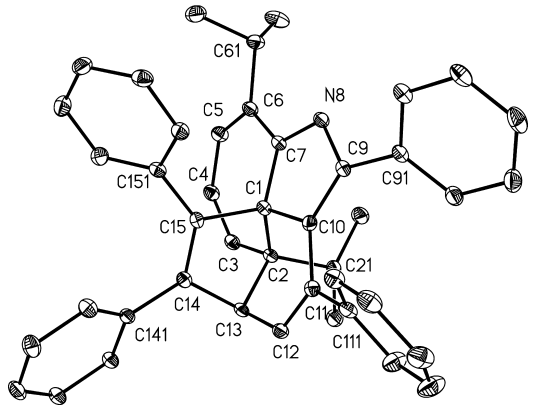

Figure 8. Molecular structure and numbering scheme of **10**. The ellipsoids represent a probability of 40%, and all H atoms are omitted for clarity. Selected bond lengths (pm): C1−C2 = 156.2(2), C1−C7 = 150.2(2), C1−C10 = 151.6(2), C1−C15 = 154.8(2), C2−C3 = 150.4(3), C2−C21 = 155.2(3), C3−C4 = 134.1(3), C4−C5 = 145.7(3), C5−C6 = 135.2(3), C6−C7 = 144.4(3), C6−C61 = 152.4(3), C7−N8 = 131.2(2), N8−C9 = 141.8(2), C9−C10 = 136.6(3), C9−C91 = 147.9(3), C10−C11 = 145.0(2), C11−C12 = 135.5(3), C11−C111 = 149.0(3), C12−C13 = 151.1(3), C13−C14 = 153.3(3), C14−C15 = 134.2(3), C14−C141 = 147.5(2), C15−C151 = 147.7(3).

Initially it was astonishing that tetracyclic imine **10** with three chiral carbon atoms formed in such a selective manner. The proposed reaction mechanism is presented in Scheme 4, offering two feasible pathways. The first reaction step is the addition of an anilide to the triple bond of diphenylbutadiyne, yielding **A**. Another alkyne inserts into the newly formed metal−carbon bond (carbometalation step to **B**). Thereafter, an intramolecular metalation yields amide **C** with a metal−nitrogen bond. The very nucleophilic amido base forms an imine, and cyclization leads to the formation of the 1,2,4,6-cycloheptratetraene derivative **D** with the negative charge at the 5-position (exemplified in Scheme 4 by an M−C bond). This carbanion reacts with H_2N-Dipp, thus regenerating the 2,6-diisopropylanilido catalyst M{N(H)Dipp} and leading to intermediate metal-free **E**. The 1,2,4,6-cycloheptratetraene fragment is very reactive, due to ring strain caused by the ketene moiety. Therefore, a cyclization reaction releases this strain and annihilates the aromatic character of the Dipp group, resulting in the tricyclic derivative **F**. Strained 1,2,4,6-cycloheptatetraenes have already attracted much interest and were prepared and preserved in an argon matrix.[34] Isomeric $C(CH)_6$ was intensively investigated by quantum chemical methods as free molecules[35] as well as a hydrocarbon captured in a molecular container.[36] These investigations show that 1,2,4,6-cycloheptatetraene is favored in comparison to a carbene embedded in a seven-membered ring.

An alternative pathway allows the protonation of **C** (and, hence, the formation of amine **G**, which is shown here with a collinear arrangement of the alkyne units requiring a specific isomerism at the C=C double bonds) combined with the re-formation of the anilido catalyst (Scheme 4). Thereafter, a Bergman cyclization leads to the formation of the diradical species **H**, which also rearranges to the tricyclic imine **F**, accompanied by a hydrogen abstraction from the amino functionality. This hydrogen transfer from the amino unit to the carbon atom is accompanied by C−C bond formation, leading to a breakup of the aromaticity of the Dipp group. The thermally controlled Bergman cyclization reactions of non-conjugated (*Z*)-hexa-1,5-diyne-3-ene yields *p*-benzyne with a triplet ground state,[37] whereas photochemically induced cyclizations follow other pathways.[38] The Bergman cyclization can be triggered by heat[39] and by internal amide functionalities,[40] occasionally also metal-mediated.[41]

A final rearrangement step yields tetracyclic 2,6-diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.0^{1,7}.0^{2,13}]-pentadeca-3,5,7,9,11,14-hexaene (**10**; 5a,9-diisopropyl-2,3,10,11-tetraphenyl-5,5*a*-dihydro-2a^1,5-ethenocyclohepta[*cd*]-isoindole), containing three chiral carbon atoms at positions 1, 2, and 13. The driving force of this final reorganization of the molecule, which divides the π system into a shorter conjugated unit (C3−C12) and an isolated C14=C15 double bond, is release of steric strain between the isopropyl group at C2 and the phenyl group at C15 (which are oriented to opposite sides of molecule **10**) as well as between neighboring phenyl substituents. Due to the strained tetracyclic structure only two enantiomers were observed and characterized by X-ray crystallography and NMR studies in order to verify the proposed structure.

During extensive NMR investigations of **10** it was observed that new resonances developed within a few days that finally grew to an approximate equimolar ratio with starting 7,15-diisopropyl-2,3,10,12-tetraphenyl-9-azatetracyclo-[8.5.0.0^{1,7}.0^{2,13}]pentadeca-3,5,7,9,11,14-hexaene (**10**). A complete conversion to 5a,9-diisopropyl-2,3,10,11-tetraphenyl-5a,6-dihydro-2a^1,6-ethenocyclohepta[*cd*]isoindole (**11**) and also purification efforts have failed as of yet. Therefore, the structure of the rearrangement product **11** was derived from NMR spectra and DFT calculations. A rearrangement mechanism is proposed in Scheme 5. This rearrangement breaks and forms a C−C bond and rearranges the conjugated π system; however, the number and size of rings as well as double bonds remain unchanged in the resulting **11**, suggesting solely reduction of intramolecular strain as the driving force for this rearrangement. Consequently the energy difference between **10** and **11** is rather small, with **11** being favored by 17.46 kJ mol^{-1} according to DFT calculations. A comparison of experimental and calculated NMR data (Table 2; for assignments see Scheme 6) shows slightly low field shifted resonances. Nevertheless, experimental parameters are in accordance with the calculated values. The trends are expressed correctly, clearly supporting the above suggested interpretation of the experimental findings.

In order to support the proposed reaction mechanisms and to deduce the importance of steric strain for the rearrangement step from **F** to **10** and from **10** to **11**, quantum chemical investigations were performed.

Quantum Chemical Investigations. Total energies E_{corr} with thermal and entropic corrections being applied as well as the number of imaginary frequencies are summarized in Table 3. We started our investigations on a simplified unsubstituted model (marked with "_**H**"; Scheme 4, R = R′ = H). Here derivative **F_H** is favored by 64.5 kJ mol^{-1} in comparison to the 1,2,4,6-cycloheptatetraene intermediate **E_H**. Surprisingly, the derivative **F_H** also is 60.5 kJ mol^{-1} lower in energy than **10_H** without isopropyl and phenyl groups. Due to the fact that unsubstituted **11_H** is only 17.4 kJ mol^{-1} lower in energy than **10_H**, derivative **F_H** represents the thermodynamically most stable product: i.e., in theory the calciate-mediated reaction of aniline with butadiyne might well end with the formation of **F_H**.

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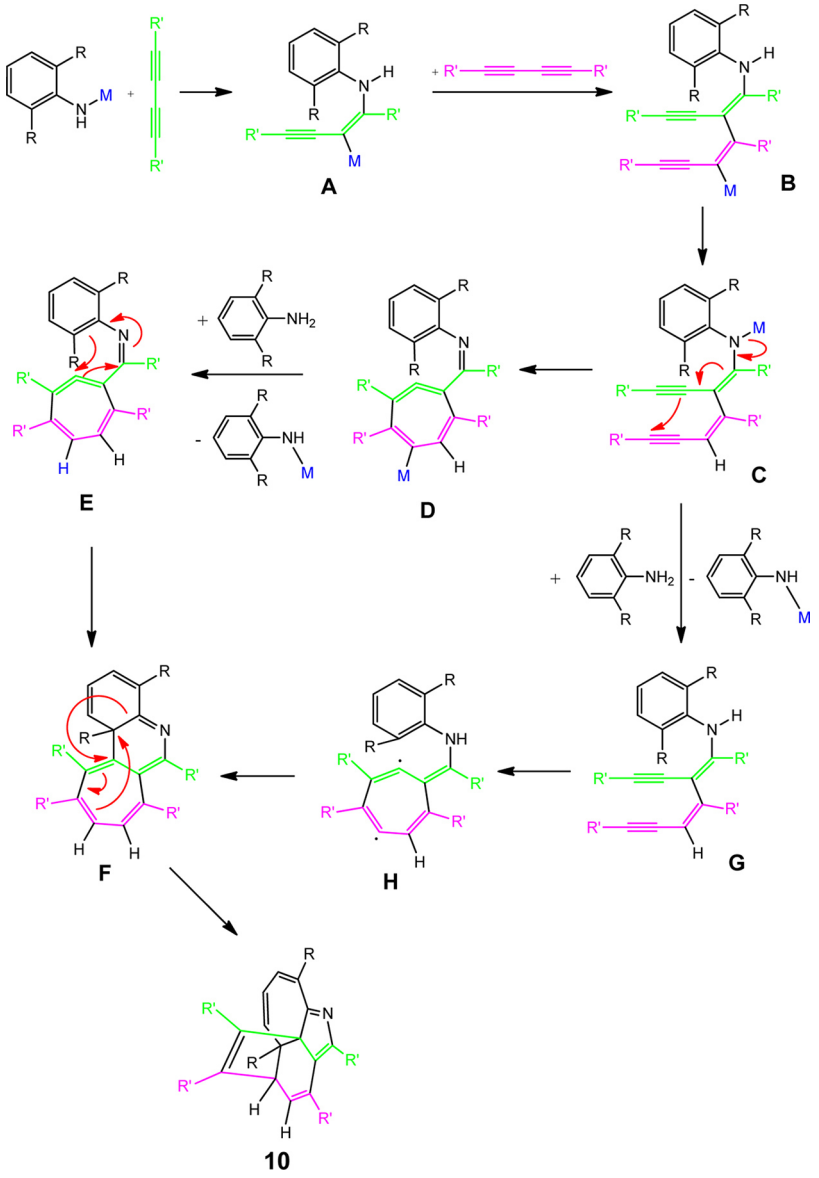
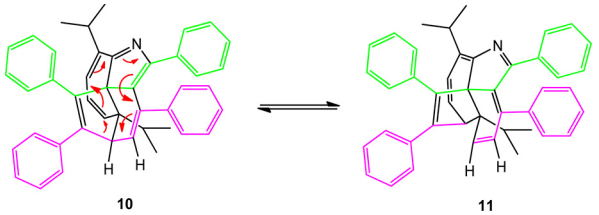
Scheme 4. Proposed Mechanism for the Calciate-Mediated Formation of Imine 10[a]



[a]R = *i*Pr, R′ = Ph; see text.

Scheme 5. Rearrangement of 10, Yielding 5a,9-Diisopropyl-2,3,10,11-tetraphenyl-5a,6-dihydro-2a^1,6-ethenocyclohepta[*cd*]isoindole (11)



Taking the substituents into account (designated with "_S"; R = *i*Pr, R′ = Ph), the situation changes significantly. In the final rearrangement from **10_S** to **11_S** the situation is similar to that for the unsubstituted derivatives, with product **11_S** again being favored by 17.6 kJ mol^{-1}. However, the substituted molecule **F_S** does not represent a minimum structure, due to massive intramolecular strain between neighboring phenyl groups. Optimization of **F_S** leads to the highly endothermic formation of an intermediate in which the neighboring phenyl substituents performed a formal [2 + 2] cycloaddition reaction, which is not a productive reaction pathway in the context of the experimentally observed reaction. Therefore, **F_S** cannot be considered as an intermediate in the formation of tetracyclic **10_S** and **11_S** but might be considered as a transition state. Moreover, the substituted intermediate **E_S** is energetically favored by 13.3 kJ mol^{-1} in comparison to **10_S** and is only 4.3 kJ mol^{-1} less stable than substituted **11_S**. The latter nevertheless is the thermodynamically most stable isomer if the substituted derivatives are considered. The alternative pathway via intermediate **G_S** is feasible from a theoretical point of view because substituted **G_S** is 48.2 kJ mol^{-1} higher in energy than **10_S**. In summary, the substitution pattern dramatically disadvantages intermediate **F_S**, although the unsubstituted derivative **F_H** represents the favored molecule if phenyl and isopropyl groups are neglected. Hence, the reaction

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Table 2. Comparison of Experimental and Calculated $^{13}C\{^1H\}$ NMR Shifts of the Central Tetracyclic Units of 10 and 11[a]

10		11	
exptl	DFT	exptl	DFT
181.0	185	170.0	174
146.2	156	160.4	168
140.3	153	137.7	145
139.2	146	136.4	144
138.9	145	135.9	142
136.2	145	133.9	142
135.6	144	131.7	141
131.6	140	131.3	141
127.5	134	127.4	138
126.8	134	127.2	138
125.5	130	126.9	133
77.8	83	66.5	72
72.8	82	57.7	64
58.3	67	48.6	58

[a]The assignment of the chemical shifts is depicted in Scheme 6.

Scheme 6. Calculated ^1H (Chemical Shifts δ, left) and ^{13}C NMR Data (Right) of 10 (Top Row) and 11 (Bottom Row)

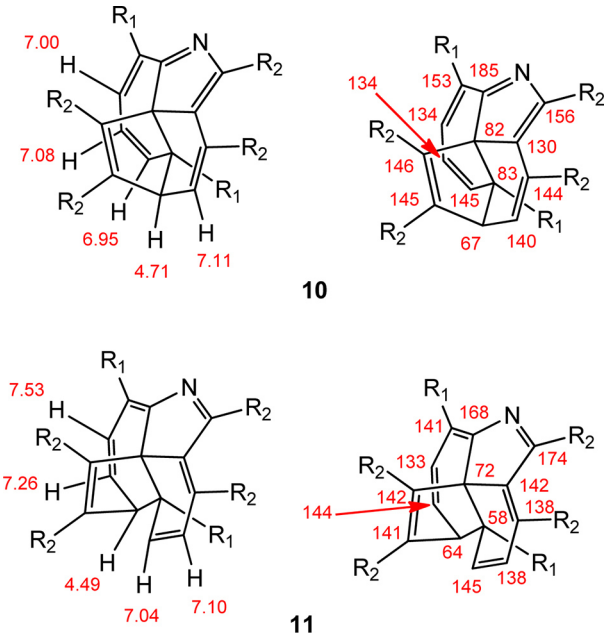

Table 3. Calculated Energies and Numbers of Imaginary Frequencies

compd[a]	E_{corr} (au)	N_{Imag}
E_H	−594.722615	0
E_S	−1754.647508	0
F_H	−594.747172	0
G_H	−594.695420	0
G_S	−1754.624103	0
10_H	−594.724130	0
10_S	−1754.642443	0
11_H	−594.730775	0
11_S	−1754.649164	0

[a]For all compounds denoted with the ending "**_H**", R = R′ = H; for all compounds denoted with the ending "**_S**", R = *i*Pr, R′ = Ph.

is pushed toward the tetracycle **10_S** in order to reduce intramolecular repulsion between adjacent phenyl groups.

CONCLUSION

Metalation of 2,6-diisopropylaniline with $K[N(SiMe_3)_2]$ yields the corresponding potassium salt $[K\{N(H)Dipp\}\cdot KN(SiMe_3)_2]$ (**1**), regardless of the applied stoichiometry. At elevated temperatures homoleptic $K\{N(H)Dipp\}$ (**5**) can be isolated. The aggregation degree of these potassium anilides strongly depends on the denticity of the neutral coligand. The addition of monobasic THF leads to polymeric $[(\mu\text{-thf})K_2\{N(H)Dipp\}_2]_\infty$ (**2**) in the solid state. Bidentate DME is able to stabilize tetranuclear $[(dme)K\{\mu\text{-}N(SiMe_3)_2\}\{\mu\text{-}N(H)Dipp\}K]_2$ (**4**), whereas in the presence of tridentate PMDETA dinuclear $[(pmdeta)K\{N(H)Dipp\}]_2$ (**3**) crystallizes. In all these solids the four-membered K_2N_2 ring is the dominating structural unit which can be interconnected via Lewis acid−base interactions between the soft potassium cations and the aryl π-systems.

These potassium anilides can be used as anilide transfer reagents. Thus, the metathetical approach with CaI_2 in tetrahydrofuran yields the corresponding calcium bis(2,6-diisopropylanilide) $[(thf)_nCa\{N(H)Dipp\}_2]$ (**6**), which can be purified and crystallized as monomeric and mononuclear complexes after addition of tri- and bidentate coligands such as pmdeta or dme, yielding $[(pmdeta)Ca\{N(H)Dipp\}_2]$ (**7**) and $[(dme)_2Ca\{N(H)Dipp\}_2]$ (**8**), respectively. Excess potassium 2,6-diisopropylphenylamide leads to the formation of the calciate $[K_2Ca\{N(H)Dipp\}_4]_\infty$ (**9**).

The potassium tetrakis(anilido)calciate **9** is highly reactive and enables a calciate-mediated hydroamination of diphenylbutadiyne with 2,6-diisopropylaniline. However, after this reaction step and a subsequent carbometalation of another butadiyne a reaction cascade leads to the formation of tetracyclic 2,6-diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo-$[8.5.0.0^{1,7}.0^{2,13}]$pentadeca-3,5,7,9,11,14-hexaene (**10**), which slowly rearranges to 5a,9-diisopropyl-2,3,10,11-tetraphenyl-5a,6-dihydro-2a^1,6-ethenocyclohepta[*cd*]isoindole (**11**).

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an argon or a nitrogen gas atmosphere using standard Schlenk techniques. Solvents were dried according to common procedures and distilled under argon or nitrogen; deuterated solvents were dried with sodium, degassed, and saturated with an inert gas. $KN(SiMe_3)_2$ was purchased from Aldrich as a solid with a purity of 95% and used without further purification. Bruker AC 200, Bruker AC 400, and Bruker AC 600 spectrometers were used to record ^1H NMR and ^{13}C NMR spectra at ambient temperature in $[D_8]$THF solutions if no other solvent is mentioned. All spectra were referenced to deuterated THF as an internal standard. The anilido complexes were extremely sensitive toward moisture and air, and therefore, combustion analysis gave no reliable results.

Synthesis of K{N(H)Dipp}K{N(SiMe$_3$)$_2$} (1). $KN(SiMe_3)_2$ (2.15 g, 10.8 mmol) was dissolved in 22 mL of toluene and the solution filtered prior to use. To this clear, colorless solution was added H_2N-Dipp (1.0 mL, 5.3 mmol) via syringe with vigorous stirring at room temperature to yield a colorless precipitate of **1**. After 3 h of stirring, pure **1** was isolated by filtration, washed twice with 7.5 mL of toluene and finally with 10 mL of pentane, and then dried in vacuo. Yield: 2.05 g (4.9 mmol, 93%). ^1H NMR: δ 6.89 (2H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.84 (1H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.41 (1H, s, N*H*), 3.12 (2H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.16 (12H, d, $^3J_{H,H}$ = 6.8 Hz, CH_3), −0.19 (18H, s, SiCH_3). $^{13}C\{^1H\}$ NMR: δ 156.6 (*i*-*C*), 129.7 (*o*-*C*), 122.1 (*m*-*C*), 106.7 (*p*-*C*), 28.2 (CH), 23.1 (*i*PrCH$_3$), 6.4 (SiCH$_3$).

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Synthesis of [(μ-thf)K$_2${N(H)Dipp}$_2$]$_\infty$ (2). This approach was performed to yield a tmeda adduct. Therefore, **1** (256 mg, 0.6 mmol) was dissolved in 1.5 mL of a 2:1 mixture of TMEDA and THF, and this reaction mixture was heated to 60 °C. Crystalline **2** was obtained overnight from this solution at ambient temperature. ^{1}H NMR: δ 6.57 (4H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.81 (2H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.62 (thf), 3.45 (2H, s, N*H*), 3.15 (4H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.78 (thf), 1.17 (24H, d, $^3J_{H,H}$ = 6.8 Hz, CH_3). ^{13}C{^{1}H} NMR: δ 157.2 (*i*-*C*), 129.6 (*o*-*C*), 122.1 (*m*-*C*), 106.3 (*p*-*C*), 68.1 (thf), 28.3 (*C*H), 26.3 (thf), 23.3 (*C*H$_3$).

Synthesis of [(pmdeta)K{N(H)Dipp}]$_2$ (3). **1** (255 mg, 0.6 mmol) was dissolved in a mixture of 2 mL of PMDETA and 0.3 mL of THF, and this solution was heated to 60 °C. Standing at room temperature yielded crystalline needles of **3**. ^{1}H NMR: δ 6.56 (4H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.78 (2H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.39 (2H, s, N*H*), 3.15 (4H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 2.29−2.44 (*C*H$_2$-pmdeta), 2.19 + 2.15 (*C*H$_3$-pmdeta), 1.16 (24H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$). ^{13}C{^{1}H} NMR: δ 157.9 (*i*-*C*), 129.5 (*o*-*C*), 122.1 (*m*-*C*), 105.8 (*p*-*C*), 58.8 + 57.3 (*C*H$_2$-pmdeta), 46.1 + 43.2 (*C*H$_3$-pmdeta), 28.3 (*C*H), 23.3 (*i*PrC*H*$_3$).

Synthesis of [(dme)K{μ-N(SiMe$_3$)$_2$}{μ-N(H)Dipp}K]$_2$ (4). **1** (316 mg, 0.8 mmol) was dissolved in 1 mL of DME. Subsequent cooling to 5 °C for about 1 week quantitatively resulted in crystalline **4**. ^{1}H NMR: δ 6.58 (4H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.83 (2H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.43 (2H, s, N*H*), 3.43 (*C*H$_2$-dme), 3.27 (*C*H$_3$-dme), 3.12 (4H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.16 (24H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$), −0.19 (36H, s, Si*C*H$_3$). ^{13}C{^{1}H} NMR: δ 156.7 (*i*-*C*), 129.7 (*o*-*C*), 122.1 (*m*-*C*), 106.7 (*p*-*C*), 72.6 (*C*H$_2$-dme), 58.8 (*C*H$_3$-dme), 28.3 (*C*H), 23.2 (*i*PrC*H*$_3$), 6.5 (Si*C*H$_3$).

Synthesis of K{N(H)Dipp} (5). H$_2$N-Dipp (0.98 mL, 5.2 mmol) was added via syringe to a clear colorless solution of KN(SiMe$_3$)$_2$ (1.033 g, 5.2 mmol) in 15 mL of toluene. The resulting suspension was heated to 100 °C for 18 h, yielding an off-white powder of **5** that contains only trace amounts of the initial amide. Yield: 1.02 g (4.7 mmol, 91%). ^{1}H NMR: δ 6.55 (2H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.75 (1H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.36 (1H, s, N*H*), 3.16 (2H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.16 (12H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$), −0.19 (1.2 H-equ, ∼7% Si*C*H$_3$). ^{13}C{^{1}H} NMR: δ 157.6 (*i*-*C*), 129.5 (*o*-*C*), 122.1 (*m*-*C*), 105.5 (*p*-*C*), 28.3 (*C*H), 23.3 (*i*PrC*H*$_3$), 6.5 (Si*C*H$_3$).

Synthesis of [(thf)$_x$Ca{N(H)Dipp}$_2$] (6). **5** (1.10 g, 5.1 mmol) and CaI$_2$ (0.75 g, 2.5 mmol) were dissolved in 15 mL of THF. Immediately, a white precipitate of KI formed that was separated by filtration over Celite after 2 h of stirring at room temperature. We note that no crystalline material could be obtained from this solution. Instead, **6** separated as an oil from diverse solvent mixtures (THF, toluene, hexane) during cooling.

Synthesis of [(pmdeta)Ca{N(H)Dipp}$_2$] (7). A 3 mL portion of a THF solution of **6** was dried in vacuo. Redissolving in 5 mL of PMDETA and 1.75 mL of THF with heating followed by cooling to −20 °C overnight yielded colorless crystalline material. ^{1}H NMR: δ 6.63 (4H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.96 (2H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.31 (2H, s, N*H*), 3.00 (4H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 2.29−2.48 (*C*H$_2$-pmdeta), 2.20 + 2.16 (*C*H$_3$-pmdeta), 1.22 (24H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$). ^{13}C{^{1}H} NMR: δ 156.9 (*i*-*C*), 130.4 (*o*-*C*), 122.1 (*m*-*C*), 108.7 (*p*-*C*), 58.8 + 57.3 (*C*H$_2$-pmdeta), 46.1 + 43.2 (*C*H$_3$-pmdeta), 29.4 (*C*H), 23.4 (*i*PrC*H*$_3$).

Synthesis of [(dme)$_2$Ca{N(H)Dipp}$_2$] (8). Crystalline **8** was obtained when oily **6** was dissolved in a few milliliters of DME and cooled to −20 °C, yielding single crystals of **8**. ^{1}H NMR: δ 6.63 (4H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 5.96 (2H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.43 (*C*H$_2$-dme), 3.31 (2H, s, N*H*), 3.28 (*C*H$_3$-dme), 3.00 (4H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.22 (24H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$). ^{13}C{^{1}H} NMR: δ 157.0 (*i*-*C*), 130.4 (*o*-*C*), 122.1 (*m*-*C*), 108.6 (*p*-*C*), 72.6 (*C*H$_2$-dme), 58.8 (*C*H$_3$-dme), 29.3 (*C*H), 23.4 (*i*PrC*H*$_3$).

Synthesis of [K$_2$Ca{N(H)Dipp}$_4$]$_\infty$ (9). **5** (814 mg, 3.8 mmol) and CaI$_2$ (280 mg, 0.9 mmol) were reacted in 10 mL of THF, and precipitation of finely divided KI was observed. THF-free crystalline material was obtained after reduction of the original volume of the calciate solution to one-third of its original volume, addition of 3 mL of toluene, and subsequent cooling to −20 °C for 2 weeks. ^{1}H NMR: δ 6.79 (8H, d, $^3J_{H,H}$ = 7.4 Hz, m-*H*), 6.31 (4H, t, $^3J_{H,H}$ = 7.4 Hz, p-*H*), 3.96 (4H, s, N*H*), 3.03 (8H, hept, $^3J_{H,H}$ = 6.8 Hz, C*H*), 1.20 (48H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$). ^{13}C{^{1}H} NMR: δ 147.4 (*i*-*C*), 131.4 (*o*-*C*), 122.6 (*m*-*C*), 113.8 (*p*-*C*), 28.3 (*C*H), 23.0 (*i*PrC*H*$_3$).

Synthesis of 2,6-Diisopropyl-9,11,14,15-tetraphenyl-8-azatetracyclo[8.5.0.0^{1,7}.0^{2,13}]pentadeca-3,5,7,9,11,14-hexaene (10). Diphenylbutadiyne (0.51 g, 2.47 mmol) was dissolved in 12 mL of THF before 2,6-diisopropylaniline (0.23 mL, 1.26 mmol) and 5 mol % of the calciate **9** were added, and the mixture was stirred overnight. A standard workup procedure including hydrolysis with 15 mL of water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from pentane gave **10** as a crude product which contained half a molecule of diphenylbutadiyne per formula unit. Final purification was performed via gradient column chromatography over silica gel, starting with pure aliphatic hydrocarbons followed by a 1:1 mixture of alkanes and ethyl acetate. The residue was recrystallized from pentane at −20 °C, yielding orange **10** (0.60 g, 1.03 mmol, 82%). Mp: 122−125 °C. NMR data without phenyl groups are as follows (for assignment see Scheme 6). ^{1}H NMR (C$_6$D$_6$, 600 MHz, 295 K): δ 6.54 (1H, d, $^3J_{H,H}$ = 6.4 Hz), 6.24 (1H, dd, $^3J_{H,H}$ = 8.6 + 12.1 Hz), 6.14 (1H, d, $^3J_{H,H}$ = 8.6 Hz), 5.81 (1H, d, $^3J_{H,H}$ = 12.1 Hz), 3.96 (1H, d, $^3J_{H,H}$ = 6.4 Hz), 3.62 (1H, hept, $^3J_{H,H}$ = 6.9 Hz, C*H*-*i*Pr), 1.89 (1H, hept, $^3J_{H,H}$ = 6.9 Hz, C*H*-*i*Pr), 1.18 (3H, d, $^3J_{H,H}$ = 6.9 Hz, *C*H$_3$-*i*Pr), 0.81 (3H, d, $^3J_{H,H}$ = 7.0 Hz, *C*H$_3$-*i*Pr), 0.80 (3H, d, $^3J_{H,H}$ = 7.0 Hz, *C*H$_3$-*i*Pr), 0.52 (3H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$-*i*Pr). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150 MHz, 295 K): δ 181.0, 146.2, 140.3, 139.2, 138.9, 136.2, 135.6, 131.6, 127.5, 126.8, 125.5, 77.8, 72.8, 58.3, 30.8, 30.8, 23.1, 22.3, 18.7, 17.7. Anal. Calcd for C$_{44}$H$_{39}$N (581.78): C, 90.84; H, 6.76; N, 2.41. Found: C, 90.80; H, 6.90; N, 2.40. MS (EI, *m*/*z* (%)): 581 (12) [M]$^+$, 379 (40) [M − diyne]$^+$, 202 (44) [diyne], 177 (100) [C$_{12}$H$_{19}$N]$^+$, 162 (68) [C$_{12}$H$_{17}$]$^+$. IR: 1599 w, 1491 w, 1443 w, 1261 m, 1177 w, 1056 w, 1027 m, 964 w, 917 w, 839 m, 756 s, 693 vs, 662 w, 608 w, 531 w, 417 w cm^{-1}.

Synthesis of 5a,9-Diisopropyl-2,3,10,11-tetraphenyl-5a,6-dihydro-2a^1,6-ethenocyclohepta[*cd*]isoindole (11). In solution product **10** rearranged with reduction of intramolecular steric strain, yielding **11**. Due to the fact that this compound always contained significant amounts of **10**, characterization was limited to NMR data. NMR parameters without phenyl groups are as follows (for assignment see Scheme 6). ^{1}H NMR (C$_6$D$_6$, 600 MHz, 295 K): δ 6.58 (1H, d, $^3J_{H,H}$ = 12.2 Hz), 6.53 (1H, d, $^3J_{H,H}$ = 9.5 Hz), 6.49 (1H, dd, $^3J_{H,H}$ = 7.6 + 12.2 Hz), 6.00 (1H, d, $^3J_{H,H}$ = 9.5 Hz), 4.64 (1H, hept, $^3J_{H,H}$ = 7.0 Hz, C*H*-*i*Pr), 3.91 (1H, d, $^3J_{H,H}$ = 7.5 Hz), 2.03 (1H, hept, $^3J_{H,H}$ = 6.9 Hz, C*H*-*i*Pr), 1.33 (3H, d, $^3J_{H,H}$ = 7.0 Hz, *C*H$_3$-*i*Pr), 1.28 (3H, d, $^3J_{H,H}$ = 7.0 Hz, *C*H$_3$-*i*Pr), 0.86 (3H, d, $^3J_{H,H}$ = 7.1 Hz, *C*H$_3$-*i*Pr), 0.73 (3H, d, $^3J_{H,H}$ = 6.8 Hz, *C*H$_3$-*i*Pr). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150 MHz, 295 K): δ 170.0, 160.4, 137.7, 136.4, 135.9, 133.9, 131.7, 131.3, 127.4, 127.2, 126.9, 66.5, 57.7, 48.6, 29.9, 29.6, 22.6, 22.6, 18.2, 17.5.

Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[42,43]

The structures were solved by direct methods (SHELXS[44]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[44]). The hydrogen atoms of compounds **2** and **10** and the hydrogen atoms bound to the amide functionalities were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered non-hydrogen atoms were refined anisotropically.[44]

Crystallographic data as well as structure solution and refinement details are summarized in Table S1 as part of the Supporting Information. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Computational Methods. Full geometry optimizations (i.e., without symmetry constraints) were carried out with the GAUSSIAN 09 program package using throughout the hybrid Hartree−Fock-DFT approach (B3LYP/6-311G(d,p)).[45−47] Stationary points of geometry optimizations were characterized to be minimum structures according to the absence of any imaginary modes by applying second-order derivative calculations. NMR spectra were calculated with the

continuous set of gauge transformations (CSGT) and the gauge-independent atomic orbital (GIAO) methods.[48] Visualization of any calculated properties was performed using the program package GAUSSVIEW.[49]

■ ASSOCIATED CONTENT

Supporting Information

Tables, figures, and CIF files giving crystallographic data of the crystal structure determinations as well as the NMR spectra of the metal anilides. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-888141 for **2**, CCDC-888142 for **3**, CCDC-888143 for **4**, CCDC-888144 for **7**, CCDC-888145 for **8**, CCDC-888146 for **9**, and CCDC-888147 for **10**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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s-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines Using a Dipotassium Tetrakis(amino)calciate Precatalyst

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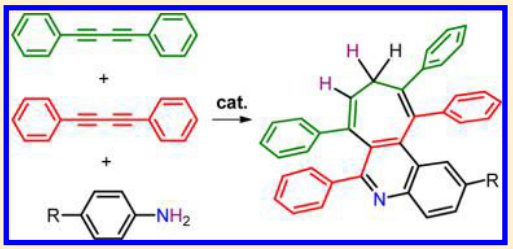
Supporting Information

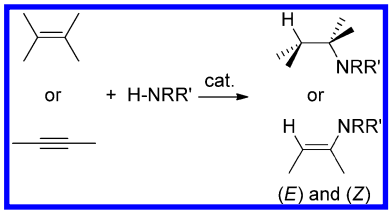
ABSTRACT: The hydroamination of diphenylbutadiyne with primary arylamines requires a reactive catalyst. In the presence of heterobimetallic $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) the performance of this reaction in THF yields 2-*tert*-butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]-quinoline (**1a**) and 2-fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (**1b**) within 3 days at room temperature when 4-*tert*-butyl- and 4-fluoroaniline, respectively, have been used. During this catalysis *o*-CH activation occurs and quinoline derivatives are formed. Blocking the *o*-CH positions by methyl groups and use of 2,4,6-trimethylaniline under similar reaction conditions leads to the formation of *N*-mesityl-7-(*E*)-((mesitylimino)(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine (**2**) containing a *β*-diketimine unit with a N−H···N hydrogen bridge. NMR experiments with labeled 4-*tert*-butylaniline verify the transfer of N-bound hydrogen atoms to the newly formed cycloheptatriene ring. If the s-block-metal-mediated hydroamination of diphenylbutadiyne is performed in refluxing THF for 6 days, *N*-aryl-2,5-diphenylpyrroles **3a**−**d** (**3a**, R = tBu, R′ = H; **3b**, R = F, R′ = H; **3c**, R = R′ = Me; **3d**, R = R′ = H) are obtained regardless of the substitution pattern of the arylamines.



INTRODUCTION

Metal-mediated hydroamination of C═C and C≡C multiple bonds with amines (Scheme 1) represents an atom-economical procedure to prepare substituted amines by addition of N−H bonds to alkenes or alkynes.[1] Generally, this process has to overcome certain challenges such as unfavorable entropic effects, electrostatic repulsion between a strongly Lewis basic amine and an electron-rich multiple bond, and lack of significant exothermic reaction enthalpy. Due to these facts several strategies have been developed to support the addition of N−H functionalities to C−C multiple bonds. On the one hand, activation of alkenes and alkynes often succeeds in the vicinity of late transition metals by back-donation of charge from the metal-centered d orbitals into π^* orbitals of the alkenes and alkynes, in agreement with the Dewar−Chatt−Duncanson model. On the other hand, the amines can be activated by oxidative addition to transition-metal complexes or by deprotonation and formation of the much more aggressive and nucleophilic amides (R_2N^-) or even imides (RN^{2-}) of early transition metals or s-block metals. The disadvantageous entropy value can be minimized by an intramolecular hydroamination reaction, leading to cyclic amines.

Scheme 1. Hydroamination of Alkenes (Top) and Alkynes (Bottom) Yielding Alkylamines and *E*/*Z*-Alkenylamines



Alkali-metal and alkaline-earth-metal complexes represent less common catalysts for diverse reasons. Organometallics of these s-block metals contain very heteropolar metal−carbon or metal−nitrogen bonds, and saltlike ionic contributions dominate the reaction pattern. In contrast to covalent bonds, electrostatic forces are nondirectional and hence control of stereochemistry has to be performed with a definite and particularly designed ligand sphere. The larger alkaline-earth-metal ions are isoelectronic with trivalent ions of the scandium group as well as tetravalent ions of the titanium group, and such d^0 metal ions are able to use d orbitals in bonding situations.[2] Due to this fact, the heavier alkaline-earth metals combine the advantageous properties of typical s-block metals (strongly ionic and highly heteropolar bonds, high reactivity, and nucleophilicity) and early transition metals (d orbital participation, Lewis acidity, catalytic behavior), with calcium being the ideal element because it is also globally abundant, available worldwide, inexpensive, and nontoxic.[3−5]

For about ten years, intramolecular calcium-mediated hydroamination of alkenes has been investigated intensely by several research groups, often employing heteroleptic com-

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plexes with one bulky protecting anion in order to partially shield the catalyst.[6−13] Intermolecular hydroamination reactions catalyzed by calcium-based complexes are much more challenging. Therefore, amines have been added to activated alkenes such as styrenes[14,15] or carbodiimides[16] as well as alkynes[14,17,18] catalyzed by amidocalcium species. These studies showed that the reactivity of the catalyst can be enhanced by using heterobimetallic potassium tetrakis(amido)calciates of the type $K_2[Ca(NRR')_4]$ in ethereal solvents. However, side -products have been observed that result from an *o*-hydrogen activation and abstraction followed by C−C bond formation (Figure 1, top).[18] Thus, the addition of diphenylamine to diphenylbutadiyne required a heterobimetallic s-block-metal catalyst, whereas the addition of more nucleophilic *N*-isopropylaniline to this butadiyne can be promoted by homometallic s-block-metal amides. In contrast to this "simple" addition of a N−H bond of a secondary amine to diphenylbutadiyne, the reaction of primary 2,6-diisopropylaniline with diphenylbutadiyne at room temperature in the presence of catalytic amounts of $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) proceeds via multiple reaction steps involving ring expansion of the 2,6-diisopropylphenyl ring to a seven-membered-ring system (Figure 1, bottom).[17] Here, 2 equiv of diphenylbutadiyne (distinguished by the colors yellow and green) react with 1 equiv of H_2N-Dipp, regardless of the applied stoichiometry.

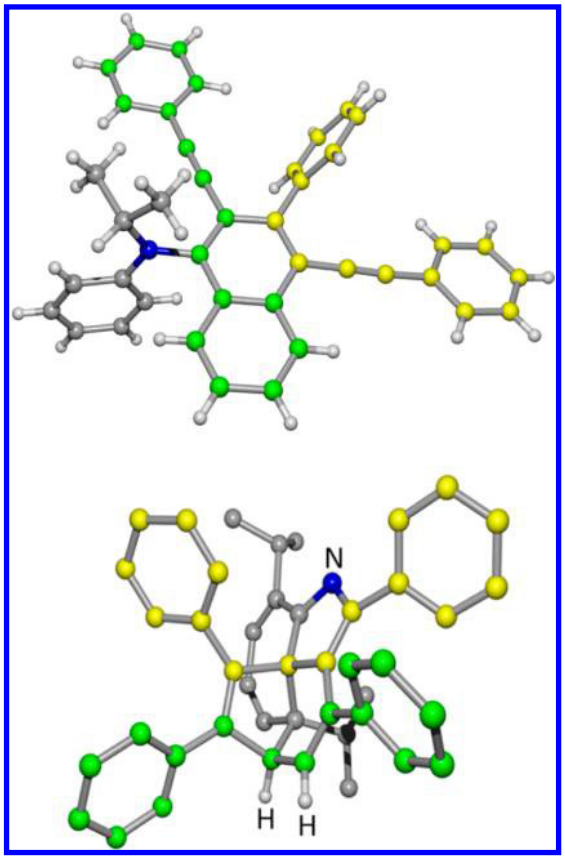


Figure 1. Products of the s-block-metal-mediated hydroamination of diphenylbutadiyne with *N*-diisopropylaniline (top) and 2,6-diisopropylaniline (bottom; only the formerly *N*-bound H atoms are depicted), containing 2 equiv of butadiyne (yellow and green) and 1 equiv of amine (C, gray; N, blue).

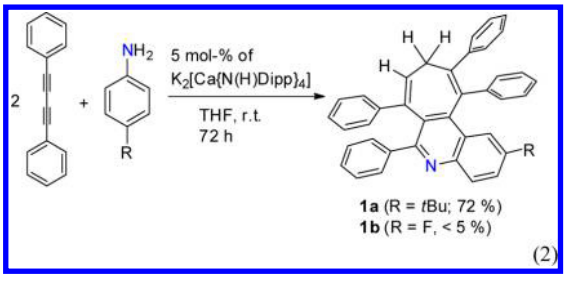
The copper-catalyzed addition of primary amines to diphenylbutadiyne gives pyrroles in high yields. This reaction requires high catalyst loads such as 25 mol % of copper(I) halide and enhanced reaction temperatures.[19]

These results initiated a detailed investigation of the reaction of primary anilines with diphenylbutadiyne in the presence of the same approved precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ under variation of the reaction conditions and the substitution pattern of the primary arylamine. We decided to maintain this precatalyst because (i) its preparation is straightforward from the metathesis reaction of KN(H)Dipp with CaI_2 (eq 1) and (ii) its purification easily succeeds by recrystallization. Furthermore, (iii) this compound crystallizes free of solvent, thus avoiding aging of the solid by uncontrolled loss of solvent molecules; hence, stoichiometric requirements (addition of a specified mole percent of $K_2[Ca\{N(H)Dipp\}_4]$ to the substrates) can easily be achieved.

$$4\mathrm{KN(H)Dipp} \xrightarrow[-2\mathrm{KI}]{+\mathrm{CaI_2}} \mathrm{K_2[Ca\{N(H)Dipp\}_4} \quad (1)$$

RESULTS AND DISCUSSION

Synthesis. In a typical procedure, equimolar amounts of diphenylbutadiyne and substituted amine were combined in tetrahydrofuran (THF) in the presence of 5 mol % of $K_2[Ca\{N(H)Dipp\}_4]$ and stirred for 3 days at room temperature. Depending on the substitution pattern, different reaction pathways have been observed. The use of 4-*tert*-butylaniline in this reaction and a hydrolytic workup procedure yields product **1a** regardless of the applied stoichiometry. This product is based on α-deprotonation steps of 4-*tert*-butylaniline and formation of a C−C bond leading to 2-*tert*-butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (**1a**); very poor yields were obtained under similar reaction conditions for the reaction of diphenylbutadiyne with 4-fluoroaniline leading to 2-fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (**1b**). The fluoro substituent withdraws electron density via the aromatic ring from the nitrogen atom, reducing the nucleophilicity of the amino functionality. Compensation of reduced reactivity by more drastic reaction conditions proved to be disadvantageous because at raised temperatures another reaction pathway was observed as discussed below, yielding a pyrrole. Nevertheless, derivatives **1a,b** both represent quinoline derivatives with annelated seven-membered rings. The reaction is depicted in eq 2, and only hydrogen atoms that are involved in the conversion are explicitly shown.



The reaction of 2,4,6-trimethylaniline with diphenylbutadiyne must proceed via a different pathway, because the ortho positions are blocked by methyl groups. In this case, a 1:1 ratio of both substrates was observed at room temperature in THF with a precatalyst load of 5 mol % of $K_2[Ca\{N(H)\text{-}Dipp\}_4]$ according to eq 3, yielding *N*-mesityl-7-(*E*)-((mesitylimino)-

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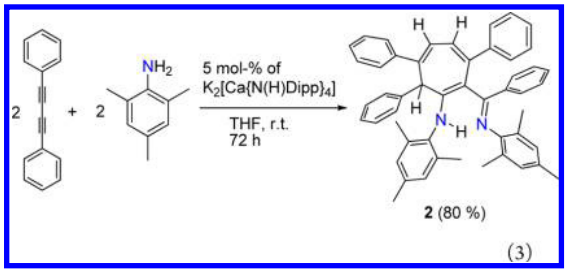
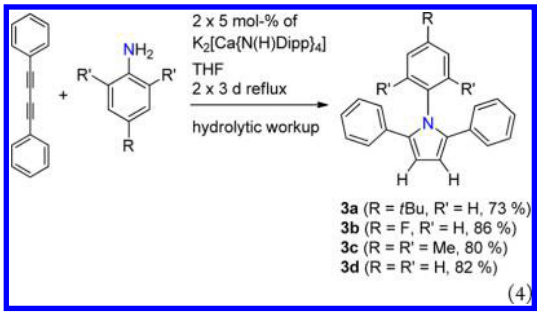


(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine (**2**). Only those hydrogen atoms are depicted that were bound at the nitrogen atom of the amine substrate. Again, a seven-membered cycloheptatriene moiety was found; however, the mesityl substituents remain intact during this transformation, in contrast to earlier findings with 2,6-diisopropylaniline yielding product **B** (Figure 1, bottom).[17]

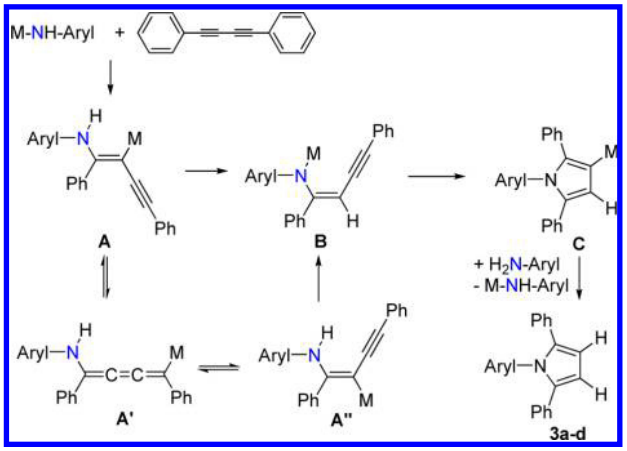
In order to study the influence of the reaction temperature, in a typical procedure diphenylbutadiyne was dissolved in THF and an equimolar amount of arylamine and 5 mol % of the catalyst $K_2[Ca\{N(H)Dipp\}_4]$ were added. This reaction mixture was stirred and refluxed for 3 days. Then another 5 mol % of $K_2[Ca\{N(H)Dipp\}_4]$ was added and heating was continued for a further 3 days. A standard workup procedure including hydrolysis with distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from pentane or toluene at 5 °C yielded colorless crystals of *N*-aryl-2,5-diphenylpyrroles **3** according to eq 4 (**3a**, R = *t*Bu, R′ = H; **3b**, R = F, R′ = H; **3c**, R = R′ = Me; **3d**, R = R′ = H).



Proposed Mechanism. In all cases, with the exception of **1b**, moderate to good yields were obtained. The precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ reacts with the primary aniline substrate, and NMR spectroscopic investigations of THF solutions containing $K_2[Ca\{N(H)\text{-}Dipp\}_4]$ and the 4-fold stoichiometric amount of 2,4,6-trimethylaniline verified the quantitative ligand exchange and formation of 2,6-diisopropylaniline. A 1:2 ratio of $K_2[Ca\{N(H)Dipp\}_4]$ and mesitylamine led to heteroleptic calciates of the general formula $K_2[Ca\{N(H)Dipp\}_{4-x}\{N(H)\text{-}Mes\}_x]$. Due to the fact that all aniline derivatives might exhibit comparable pK_a values, it can be concluded that the bulkier amide is replaced by the smaller amide in order to minimize intramolecular strain of the calciate anion mainly provoked by the ortho substituents.

The catalytic reaction starts with the addition of a metal−nitrogen bond to one C≡C triple bond as shown in Scheme 2 (nucleophilic attack of an amide at an alkyne) yielding intermediate **A**. In this scheme, M symbolizes the s-block metal and hence the anionic site. The reactivity of homometallic calcium amides is not sufficient to mediate this hydroamination. Therefore, we employed the already known strategy to significantly enhance the reactivity by formation of a

Scheme 2. Proposed Mechanism of the s-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines at High Temperatures Yielding *N*-Aryl-2,5-diphenylpyrroles



heterobimetallic catalyst system.[17,18] *E*/*Z* isomerization is possible via the cumulene isomer **A**′, which can isomerize to either a trans (**A**) or a cis orientation (**A**″) of the anionic site and the remaining alkyne moiety. Such cumulene systems have also been suggested during calcium-mediated hydrophosphanylation of diphenylbutadiyne with diphenylphosphane in order to explain isomer mixtures.[20] After the initial reaction step, intramolecular metalation transfers the *N*-bound hydrogen to the alkenyl moiety and amide **B** is formed. During the high-temperature route an intramolecular addition to the second alkyne unit occurs and the pyrrole derivative **C** is formed. The reaction of this intermediate species with another arylamine regenerates the catalyst, and the formation of pyrroles **3a**−**d** is completed.

In contrast to this straightforward pathway for the synthesis of pyrroles **3a**−**d**, the low-temperature route proceeds via an insertion of another diphenylbutadiyne molecule into the metal−carbon bond of the primary reaction product (carbometalation step, Scheme 3) yielding intermediate **D**. For the sake of clarity the diphenylbutadiyne units are distinguished by different colors in this scheme. An intramolecular metalation reaction forms amide **E**. Now, two reaction routes seem to be feasible to explain the formation of **1** (via *o*-CH activation) and **2** (via addition of a second arylamine). These compounds are depicted in Figure 2, also clarifying the origin of the structural moieties. The closed-shell ionic mechanism involves the formation of the 1,2,4,6-cycloheptatetraene intermediate **F**. Such species exhibit ring strain; nevertheless, unsaturated ring systems of this kind have already been studied in a solid matrix[21] and by quantum chemical investigations, also considering other isomers such as phenylcarbene, bicyclo[3.2.0]hepta-1,3,6-triene, bicyclo[3.2.0]-hepta-3,6-diene-2-ylidene, bicyclo[3.2.0]hepta-2,3,6-triene, and bicyclo[4.1.0]heptatriene.[22] Furthermore, a cyclotetramer of such a strained cycloheptatetraene derivative has been characterized by an X-ray crystal structure determination.[23] Despite the fact that ring strain is present in cycloheptatetraenes, these derivatives also represent $4n$ π-Möbius aromatic systems.[24] Intermolecular metalation by an arylamine regenerates the catalyst and leads to the formation of **G**.

In this bicyclic intermediate **G** the allene moiety attacks the *o*-CH group leading to compound **1**. Absence of *o*-CH

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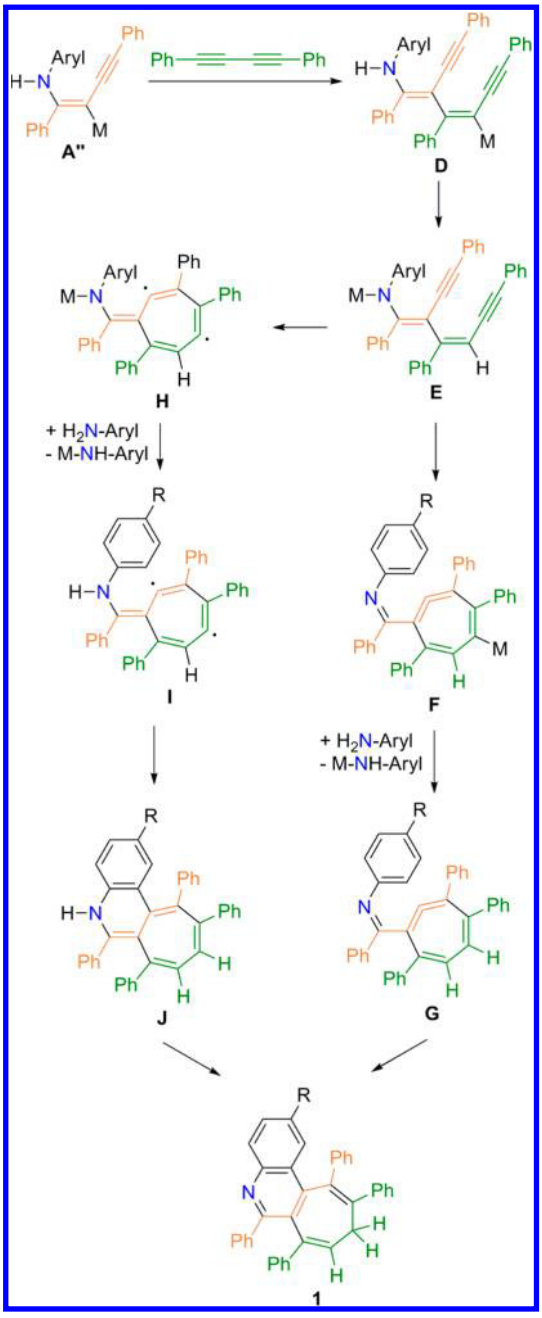
Scheme 3. Proposed Mechanism of the s-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines at Room Temperature via a 1,2,4,6-Cycloheptatetraene Intermediate and via a Bergman Cyclization Route[a]



[a]The diphenylbutadiyne units are distinguished by the colors orange and green.

fragments and bulkier N-bound aryl groups favor the formation of isomer **G′** (Scheme 4), leading to an alternative reaction pattern. Here, the 1,4-addition of an arylamine to the cycloheptatetraene ring leads to the formation of compound **2**.

An alternative pathway contains the Bergman cyclization leading to diradical **H**. Again the catalyst is re-formed by an intermolecular reaction with an arylamine yielding intermediate **I**. This radical can attack either at a *o*-CH group (yielding **1**) or—in the case that such a functionality is absent—another amine substrate, leading to compound **2** as shown in Scheme 4.

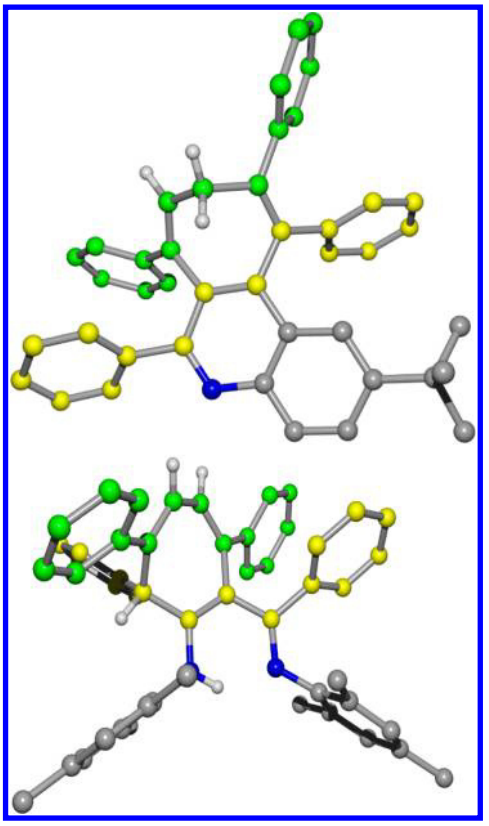
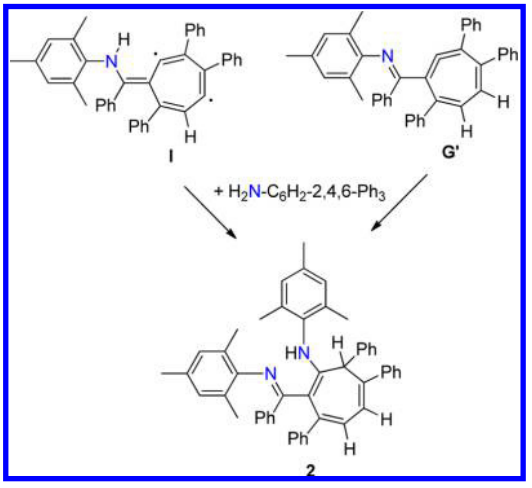


Figure 2. Stick-and-ball presentations of **1** (top) and **2** (bottom). The structural building blocks are distinguished by different colors: the initial diphenylbutadiyne moieties are shown in yellow and green and the arylamines in gray (C atoms) and blue (N atom). Only those H atoms are drawn (light gray) that are involved in chemical transformations or are bound at a nitrogen atom.

Scheme 4. Proposed Final Mechanistic Steps for the Formation of 2 Starting from I or G′[a]



[a]**G′** is the *E* isomer of **G**.

The fact that homometallic calcium bis(amide) does not mediate these hydroamination reactions raises the question of the cooperation of potassium and calcium in the catalyst system. In the solid state $K_2[Ca\{N(H)Dipp\}_4]$ forms a coordination polymer consisting of $[Ca\{N(H)Dipp\}_4]^{2-}$ anions interconnected by potassium cations.[17] It can be assumed that in solution the calciate anions are maintained.

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In these calciate anions electrostatic repulsion between the amido substituents enhances the Ca−N bond lengths and, hence, the nucleophilicity and reactivity of the amido groups. This consideration suggests that M in the schemes might be a calciate fragment. The role of the potassium ions remains unclear and speculative. Potassium ions are considered as soft Lewis acids, being able to coordinate to rather hard (such as ethers) and preferably to soft Lewis bases such as aromatics and extended π systems. Nevertheless, it remains speculative to what extent this coordination behavior of K^+ supports the catalytic hydroamination via coordination to any of the reported intermediates. Due to the fact that rather high yields of the products were obtained and that cycloheptatetraene derivatives have already been accessible experimentally, we favor the mechanism via the cycloheptatetraene intermediates. In addition, we would expect diverse derivatives for the radical mechanism due to reactions of the radical with solvent molecules and still present arylamine substrates.

NMR Experiments. The ^{1}H NMR spectrum of **1a** (R = *t*Bu) clearly shows a characteristic ABX coupling pattern for the hydrogen atoms at the seven-membered ring leading to three doublets of doublets (Figure 3) with a pseudotriplet for the CH

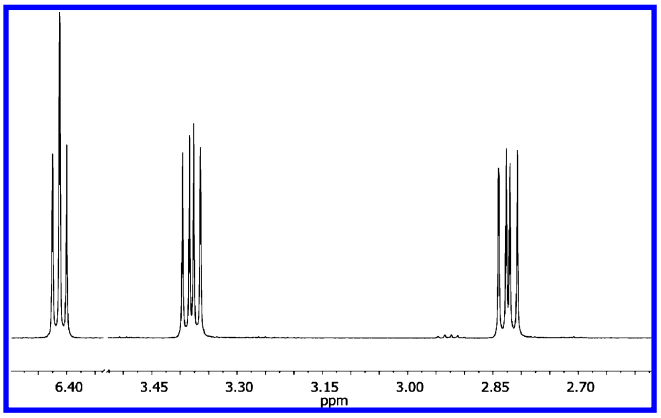

Figure 3. ^{1}H NMR resonances of the newly formed methylene unit of the seven-membered ring of compound **1a**. The coupling pattern clearly verifies the magnetic nonequivalence of the H atoms.

resonance at δ 6.41 ppm due to very similar vicinal coupling constants. The H atoms of the methylene fragment are magnetically inequivalent with a geminal coupling constant of $^2J_{HH}$ = 11.6 Hz, verifying the nonplanarity of the cycloheptatriene unit.

In order to support the reaction mechanism, we repeated the preparation of this compound with partially N-deuterated 4-*tert*-butylaniline with a deuteration degree of 75%. This approach should yield **1a** in addition to its partially deuterated derivatives. The coupling pattern in the ^{1}H NMR spectrum at the CH signal at δ = 6.41 ppm enables the assignment and determination of the positions of deuterium atoms (Figure 4). The coupling pattern of the endocyclic =CH−CH_2− fragment allows the assignment to the moieties CH−CH_2, CH−CHD, and CH−CDH. The intensity ratio of the resonances excludes the formation of CH−CD_2 units, which would suggest a bimolecular reaction mechanism. This coupling pattern and the resonances of the neighboring methylene group (see the Supporting Information) clearly show that there exists no preference for deuteration at either position and hence no stereocontrol for the transfer of the *o*-hydrogen atom of the 4-

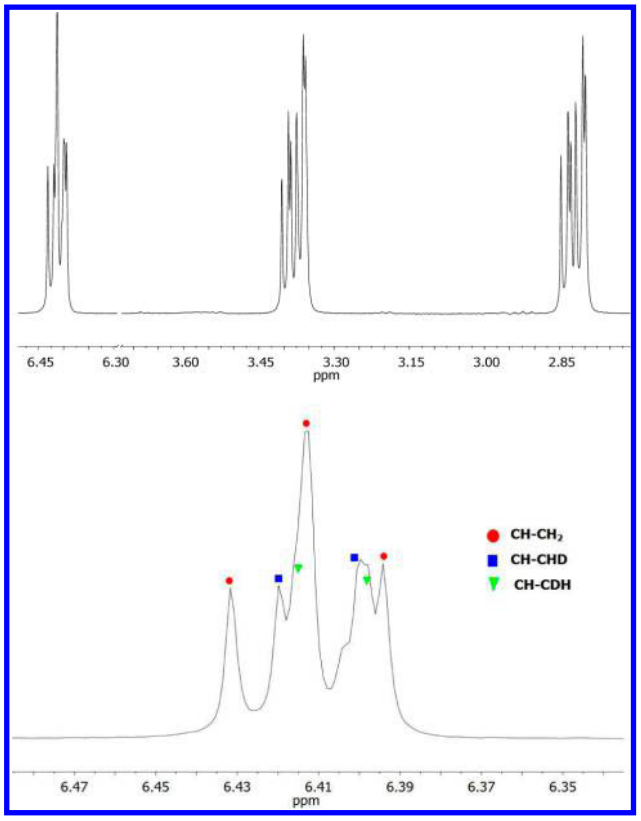

Figure 4. ^{1}H NMR spectrum of the CH fragment of the seven-membered ring of partially deuterated **1a** (top), with assignment to differently deuterated derivatives (bottom).

tert-butylphenyl group to the seven-membered ring yielding the methylene group.

Compound **2** represents a β-diketimine derivative with an annelated unsaturated seven-membered ring. This structural fragment gives rise to a low-field-shifted resonance for the N−H···N hydrogen bridge with a chemical shift of δ 12.85 ppm. In Figure 5 the ^{1}H NMR spectrum of the methyl region is

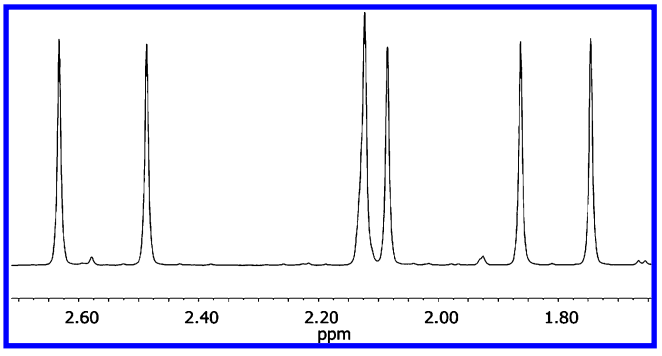

Figure 5. ^{1}H NMR resonances of the methyl substituents of the mesityl groups, showing that the 2,6-positions are magnetically nonequivalent, which suggests a hindered rotation of the mesityl groups around the N−C bonds.

depicted. All methyl groups are chemically different, which has been explained by hindered rotation around the C−N bonds. The nonequivalence of the *o*-methyl groups of each mesityl substituent is a consequence of the chiral carbon atom of the seven-membered cycloheptatriene ring.

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Molecular Structures. The molecular structure and numbering scheme of *N*-mesityl-2,5-diphenylpyrrole (**3c**) are depicted in Figure 6. Due to steric reasons the N-bound aryl group is oriented nearly perpendicular to the pyrrole ring with an angle of 69.2° between these planes. Expectedly, the π system of the pyrrole ring leads to short bonds and charge delocalization to a large extent. Endocyclic C1−C2, C2−C3, and C3−C4 bond lengths differ by less than 3 pm and have an average value of 138.9 pm. The exocyclic C1−C20 and C4−C5 bond lengths, with an average distance of 147.2 pm, are characteristic for single bonds between sp^2-hybridized carbon atoms. 1,2,5-Triphenylpyrrole (**3d**) exhibits crystallographic C_2 symmetry and shows very similar structural parameters (see the Supporting Information). This measurement at −140 °C leads to results very similar to those of the crystal structure determination at room temperature.[25]

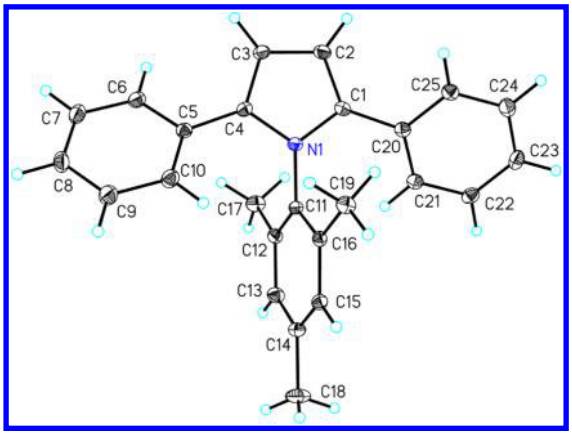

Figure 6. Molecular structure and numbering scheme of **3c**. The ellipsoids represent a probability of 30%, and H atoms are shown with arbitrary radii. Selected bond lengths (pm): N1−C1 139.1(2), N1−C4 139.3(2), N1−C11 144.4(2), C1−C2 138.1(2), C2−C3 140.7(2), C3−C4 137.8(2), C1−C20 147.6(2), C4−C5 146.8(2). Selected bond angles (deg): C1−N1−C4 109.0(1), N1−C1−C2 107.5(1), C1−C2−C3 107.9(1), C2−C3−C4 108.4(1), N1−C4−C3 107.3(1), C1−N1−C11 125.6(1), C4−N1−C11 125.1(1), N1−C1−C20 124.7(1), C2−C1−C20 127.8(1), N1−C4−C5 125.3(1), C3−C4−C5 127.4(1).

Verification of the compositions of **1a**,**b** and **2** as shown in Figure 2 was also successful by X-ray diffraction experiments on single crystals. Molecular structures and numbering schemes of **1a**,**b** are presented in Figures 7 and 8, respectively. The numbering schemes of both compounds are identical, and a comparison of selected bond lengths is given in Table 1. These compounds are built from two butadiyne molecules (atoms C1A−C16A and C1B−C16B) and one 4-*tert*-butylaniline (N1A, C17A−C26A) or 4-fluoroaniline molecule (N1A, F1A, C17A−C22A), respectively. The quinoline fragments show balanced bond lengths which are comparable to those of unsubstituted quinoline.[26] Substituents at the quinoline nucleus of **1a**,**b** lead to a slight lengthening between those carbon atoms carrying substituents. The phenyl groups are oriented nearly perpendicular to the ring systems; hence, no interaction between the aromatic phenyl groups and the π-systems of the seven-membered ring can be expected and characteristic C−C single bond values around 149 pm were observed.

The molecular structure and numbering scheme of compound **2** are shown in Figure 9. This compound is built from two butadiyne (atoms C1A−C4A and C1B to C4B) and two 2,4,6-trimethylaniline molecules (N1A and C17A−C25A as well as N1B and C17B−C25B). Compound **2** contains the chiral C4B atom, but due to the centric monoclinic space group the crystalline state consists of a racemate. The structure-dominating moiety is the N1A−C1B−C2B−C3B−N1B fragment with significant charge delocalization and a N1B−H···N1A hydrogen bridge (N1A···N1B distance 265.7(3) pm). The C1A−C2B bond length shows a characteristic single-bond value for sp^2-hybridized carbon atoms excluding π interaction between the β-diketimine unit and the remaining π bonds of the seven-membered ring. This hydrogen bridge also explains why only the *E* isomer of the N1A═C1B imine unit is observed.

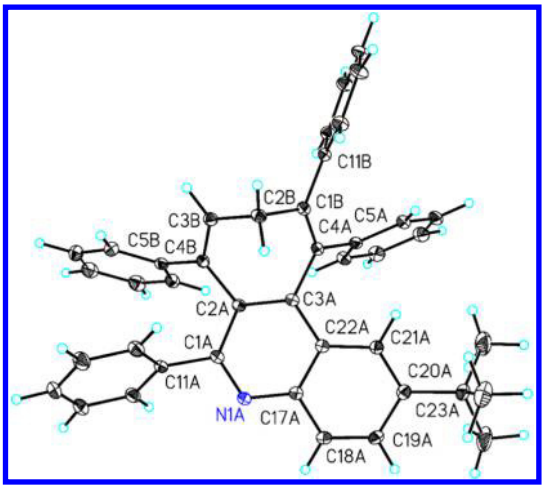

Figure 7. Molecular structure and numbering scheme of **1a**. The ellipsoids represent a probability of 30%, Hand atoms are shown with arbitrary radii. Selected bond lengths are given in Table 1.

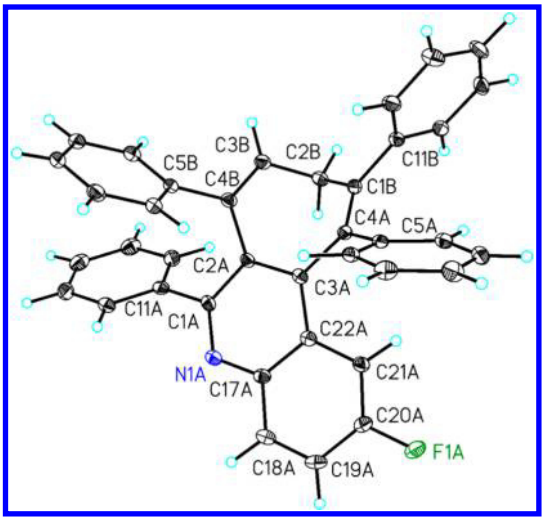

Figure 8. Molecular structure and numbering scheme of **1b**. The ellipsoids represent a probability of 30%, and H atoms are shown with arbitrary radii. Selected bond lengths are given in Table 1.

CONCLUSION

The s-block-metal-mediated hydroamination of diphenylbutadiyne with primary amines in THF requires the presence of 5−10 mol % of heterobimetallic $K_2[Ca\{N(H)Dipp\}_4]$; homometallic calcium bis(amides) did not initiate the hydroamination under similar reaction conditions. The substitution pattern of the arylamines and the reaction conditions strongly influence the reaction pathway. At high temperatures in

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Table 1. Comparison of Selected Bond Lengths (pm) of 2-*tert*-Butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (1a) and 2-Fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (1b)

bond	**1a** (R = *t*Bu)	**1b** (R = F)
N1A−C1A	131.4(2)	131.4(3)
N1A−C17A	137.1(2)	138.0(3)
C17A−C18A	140.8(2)	141.5(3)
C17A−C22A	141.6(2)	141.5(3)
C18A−C19A	137.0(2)	137.5(4)
C19A−C20A	141.4(2)	138.7(4)
C20A−C21A	138.5(2)	136.4(3)
C20A−R	153.2(2)	136.3(3)
C21A−C22A	141.6(2)	141.9(3)
C1A−C2A	144.4(2)	144.2(3)
C1A−C11A	149.1(2)	149.6(3)
C2A−C3A	139.5(2)	139.5(3)
C2A−C4B	148.6(2)	148.3(3)
C3A−C4A	149.2(2)	148.6(3)
C3A−C22A	144.6(2)	146.2(3)
C4A−C5A	149.4(2)	149.4(3)
C4A−C1B	135.6(2)	135.8(3)
C1B−C2B	151.8(2)	151.1(3)
C1B−C11B	149.0(2)	149.3(3)
C2B−C3B	150.3(2)	150.5(3)
C3B−C4B	133.8(2)	132.8(3)
C4B−C5B	149.0(2)	149.2(3)

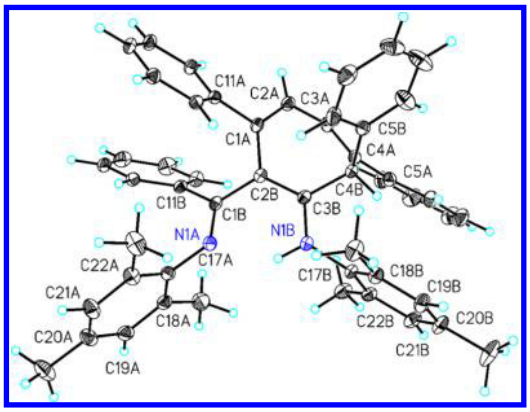

Figure 9. Molecular structure and numbering scheme of **2**. The ellipsoids represent a probability of 30%, and selected H atoms are shown with arbitrary radii. Selected bond lengths (pm): N1A−C17A 142.9(3), N1A−C1B 129.5(3), N1B−C17B 143.2(3), N1B−C3B 135.7(3), N1B−H 88(3), C1A−C2A 135.8(3), C1A−C2B 147.2(3), C1A−C11A 149.0(3), C2A−C3A 143.9(3), C3A−C4A 134.7(3), C4A−C5A 148.4(3), C4A−C4B 152.8(3), C1B−C2B 146.9(3), C1B−C11B 150.6(3), C2B−C3B 139.1(3), C3B−C4B 151.6(3), C4B−C5B 153.9(3).

refluxing THF the formation of *N*-aryl-2,5-diphenylpyrroles succeeds with moderate to high yields. A 2-fold addition of metal−nitrogen bonds to both C≡C triple bonds yields pyrrole rings with an aromatic character.

In contrast to the high-temperature route, the s-block-metal-mediated reaction of diphenylbutadiyne with arylamines at room temperature strongly depends on the substituents in ortho positions. During this reaction an amide reacts with two diphenylbutadiyne molecules. Cyclization leads either to a cyclohepta-1,2,4,6-tetraene intermediate or, via Bergman cyclization, to a methylidene−cycloheptatrienediyl radical. These highly reactive intermediates attack *o*-CH functionalities of the arylamine unit, leading to a quinoline derivative with a 2:1 ratio of butadiyne to arylamine. If *o*-CH groups are not available, another reaction pathway is pursued and the reactive intermediate traps another 1 equiv of arylamine, yielding a *β*-diketimine derivative which is annelated to a seven-membered ring. This *β*-diketimine crystallizes in the ene−amine form with a N−H···N hydrogen bridge and shows no significant conjugation with the attached multiple bonds of the annelated seven-membered ring. The performance of this s-block-metal-mediated hydroamination of diphenylbutadiyne at room temperature allows the synthesis of quinolone derivatives in the presence of *o*-CH functionalities.

Special attention has to be given to the advantageous properties of the catalyst system. The reaction of 4 equiv of KN(H)Dipp with calcium iodide in THF yields solvent-free $K_2[Ca\{N(H)Dipp\}_4]$.[17] The potassium ions bind to the amido anions and to the *π* systems of the aryl groups, leading to a coordination polymer in the solid state. Nevertheless, this complex is soluble in ethers. On the one hand, the rather bulky isopropyl groups in ortho positions prevent formation of ether adducts which commonly tend to slowly lose these neutral coligands upon standing and handling. Partial loss of coligands leads to weathering of the crystalline material and makes it difficult to exactly meet the stoichiometry. On the other hand, these isopropyl groups enhance intramolecular steric strain which can be released by a ligand exchange reaction and, therefore, in solution a fast substitution of the 2,6-diisopropylanilide anion by smaller amide ligands occurs. This initial amide exchange, which is much faster than the addition to the alkyne moieties, is the reason that $K_2[Ca\{N(H)Dipp\}_4]$ represents an ideal precatalyst for any hydroamination of diphenylbutadiyne with sterically less demanding primary arylamines. It is a common observation that heterobimetallic s-block-metal compounds often adopt reactivities different from those of their homometallic constituents.[5,27−30] These mixed-metal complexes form metalates[27,28] which are in some cases addressed as inverse crowns[29] and turbo Grignard or turbo Hauser reagents.[30]

In conclusion, thermodynamic control (in boiling THF) of s-block-metal-mediated hydroamination of diphenylbutadiyne with primary arylamines employing $K_2[Ca\{N(H)Dipp\}_4]$ yields *N*-aryl-2,5-diphenylpyrroles regardless of the bulkiness of the N-bound aryl groups, whereas kinetic control (at room temperature) leads to rather complex reaction pathways depending on the ortho substituents of the arylamines, where the formation of unsaturated seven-membered rings represents a key feature.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. The solvent was dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. The yields given are not optimized. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC 400 and AC 600 spectrometers. Chemical shifts are reported in parts per million relative to $SiMe_4$ as an external standard. The residual signals of the deuterated solvents $[D_8]$THF and CD_2Cl_2 were used as internal standards. The solvent-free and recrystallized precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ was prepared according to a literature procedure.[17] A specific amount of this compound was dissolved in anhydrous THF, and aliquots of this solution were added to the reaction mixtures. This procedure allowed

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us to easily add definite amounts of precatalyst to the substrates under strictly anaerobic conditions. All substrates were purchased from Sigma-Aldrich, Merck, or Alfa Aesar and used without further purification.

General Procedure for the Synthesis of 2-Substituted 6,7,10,11-Tetraphenyl-9*H*-cyclohepta[*c*]quinolone (1; R = tBu, F). A 2 equiv amount of diphenylbutadiyne was dissolved in THF. Thereafter, 1 equiv of 4-*tert*-butylaniline and 5 mol % (with respect to the butadiyne) of the catalyst $K_2[Ca\{N(H)Dipp\}_4]_\infty$ were added. This solution was stirred for 3 days at room temperature. After hydrolysis with distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from a mixture of dichloromethane and pentane at 5 °C, colorless crystals were isolated from an orange mother liquor.

Synthesis of 2. Diphenylbutadiyne (0.3 g 1.48 mmol) was dissolved in 15 mL of THF. Then, 0.21 mL of 2,4,6-trimethylaniline (0.2 g, 1.48 mmol) and 5 mol % of the calciate catalyst $K_2[Ca\{N(H)Dipp\}_4]_\infty$ were added. This reaction mixture was stirred for 3 days at oom temperature. A standard workup procedure included hydrolysis with 15 mL of distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from a mixture of dichloromethane and pentane at 5 °C, yielding colorless crystals in a reddish brown mother liquor. Yield: 0.4 g, 0.59 mmol, 80%.

General Procedure for the Synthesis of *N*-Aryl-2,5-diphenylpyrroles 3. Diphenylbutadiyne (0.3 g 1.48 mmol) was dissolved in 17 mL of THF before 4-fluoraniline (0.164 g, 1.48 mmol) and 10 mol % of the calciate $K_2[Ca\{N(H)Dipp\}_4]_\infty$ (5 mol % at the beginning and 5 mol % after 3 days) were added, and the reaction mixture was heated for 6 days at 60 °C. Thereafter, the solution was hydrolyzed with 15 mL of distilled water and extracted with diethyl ether and the separated ether phase dried with sodium sulfate. Recrystallization from pentane at 5 °C yielded a colorless solid (0.40 g, 1.27 mmol, 85.8%) in an orange mother liquor.

X-ray Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple scans.[31−33] The structures were solved by direct methods (SHELXS)[34] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[34] The hydrogen atoms (with the exception of methyl groups C24, C25, and C26 of **1a** and **2**) were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.[34] Crystallographic data as well as structure solution and refinement details are summarized in the Supporting Information. The programs XP (Siemens Analytical X-ray Instruments, Inc.)[35] and POV-Ray[36] were used for structure representations.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, a table, and CIF files giving preparative details and physical data of all reported compounds and crystallographic data of the crystal structure determinations as well as the NMR spectra of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00449. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1062187 for **1a**, CCDC-1062188 for **1b**, CCDC-1062189 for **2**, CCDC-1062190 for **3c**, and CCDC-1062191 for **3d**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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Hydroamination of diphenylbutadiyne with secondary *N*-methyl-anilines using the dipotassium tetrakis(2,6-diisopropylanilino)calciate precatalyst†

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The approved precatalyst $[K_2Ca\{N(H)Dipp\}_4]$ was employed to study the hydroamination of diphenylbutadiyne with *N*-methyl-anilines in tetrahydrofuran at room temperature. The hydroamination occurs regioselectively within a few hours yielding (*N*-methyl)-(*N*-aryl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine with phenyl (**1a**), 4-tolyl (**1b**) and 4-fluorophenyl groups (**1c**). In all cases a mixture of *E*- and *Z*-isomers is obtained. The second hydroamination step requires drastically extended reaction times and is successful only for the reaction of diphenylbutadiyne with *N*-methyl-aniline and *N*-methyl-4-fluoroaniline giving 1,4-diphenyl-1,4-bis(*N*-methyl-anilino)buta-1,3-diene [R = H (**2a**) and F (**2c**)]; a mixture of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-isomers is obtained. The X-ray structures of *E*-**1a**, *E*-**1b** and *E*-**1c** show a slightly shortened N–C bond to the alkene moieties. Due to enhanced steric strain the anilino units of *Z*,*Z*-**2c** and *Z*,*Z*-**3** turn away from the butadiene unit and consequently, the lone pair at the planar nitrogen atoms slightly interacts with the adjacent aryl groups.

Introduction

Hydroamination of unsaturated hydrocarbons – the addition of N–H bonds to alkenes and alkynes – represents a highly eligible atom-economical reaction for the synthesis of alkyl- and alkenylamines. However, this reaction is disadvantageous for several reasons. (i) The attack of an electron-rich amine at an electron-rich C–C multiple bond requires to overcome electrostatic repulsion. (ii) In addition, this reaction generally is only very slightly exothermic and, hence, lacks a strong driving force. (iii) Furthermore, the addition of an amine to an alkene or alkyne is entropically disfavored due to the reduction of degree of freedom. (iv) The large energy difference between the N–H σ-bond and the C–C π-bond also hampers the facility of this addition reaction. Therefore, several strategies have been developed to overcome the challenges of the hydroamination of unsaturated hydrocarbons. Activation of the alkenes or alkynes often succeeds in the vicinity of late transition metals.[1] Deprotonation of primary and secondary amines and formation of amides and imides enhance the reactivity of the amines. This method is performed with s-block metals, lanthanoides and early transition metal reagents.[2–4] Intramolecular hydroamination leads to cyclic amines and imines and allows the reduction of the disadvantageous entropy effect.

Very recently the validity of heavier alkaline earth metal reagents in hydroamination reactions has been demonstrated.[3] These s-block metals combine the advantageous properties of early transition metals (Lewis acidic metal ions, catalytic behavior, availability of d-orbitals) and typical s-block metals (strongly heteropolar bonds, high nucleophilicity, electrostatic factors dominate the bonding). In this row calcium represents the most attractive metal because it is globally abundant, available world-wide, inexpensive, and non-toxic. In order to avoid the entropic challenge, first studies dealt with intramolecular calcium-mediated hydroamination of alkenes.[5] The intermolecular hydroamination with reagents of the heavier alkaline earth metals required activated alkenes.[6] The intermolecular addition of N–H bonds across alkynes seemed to be less inhibited.[6,7] The hydroamination of diphenylbutadiyne proceeded smoothly with *N*-alkyl-anilines whereas the addition of diphenylamine required a significantly more reactive catalyst system such as the dipotassium calciate $[K_2Ca(NPh_2)_4]$.[7]

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†Electronic supplementary information (ESI) available: NMR spectra of all new compounds and details of the quantum chemical studies. CCDC 1426897 for *E*-**1a**, 1426898 for *E*-**1b**, 1426899 for *E*-**1c**, 1426900 for *E*,*E*-**2a**, 1426901 for *Z*,*Z*-**2c**, and 1426902 for *Z*,*Z*-**3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03818a

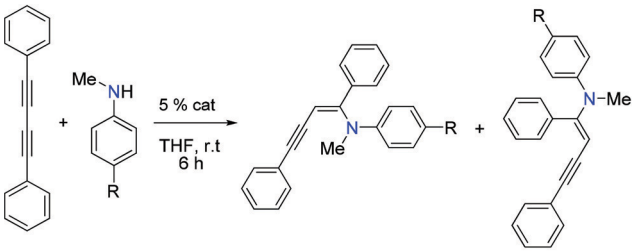
During these calcium-mediated hydroamination reactions only the singly hydroaminated butadiynes were isolated whereas the second C≡C triple bond remained intact. A surprisingly different behavior was observed for the reaction of primary anilines with diphenylbutadiyne in the presence of a calciate-based catalyst system.[8] Depending on the reaction temperature and time either a twofold addition to diphenylbutadiyne (yielding 2,5-diphenylpyrroles) was observed or a rather complex reaction sequence led to multicyclic compounds. In either case, both C≡C triple bonds were attacked by N–H functionalities.[8] In the latter reaction cascade the substitution pattern of the aniline played a significant role in the constitution of the final product. In all these calcium-mediated catalytic processes, the calciate $[K_2Ca\{N(H)Dipp\}_4]$ (Dipp = C_6H_3-2,6-iPr_2) proved to represent an ideal choice because this compound crystallized without ligated ether bases and consequently, it can be weighed, handled and stored under an inert atmosphere without aging of the crystalline material due to loss of ethereal coligands. In addition, smaller amines easily replace the bulky Dipp-NH_2 *via* transamination reactions in order to release steric pressure.

Based on the finding that anilines react with both C≡C triple bonds of diphenylbutadiyne we reexamined the hydroamination of this hydrocarbon with secondary *N*-methylanilines of the type HN(Me)(C_6H_4-4-R) (R = H, Me, F).

Results and discussion

Singly hydroaminated diphenylbutadiyne

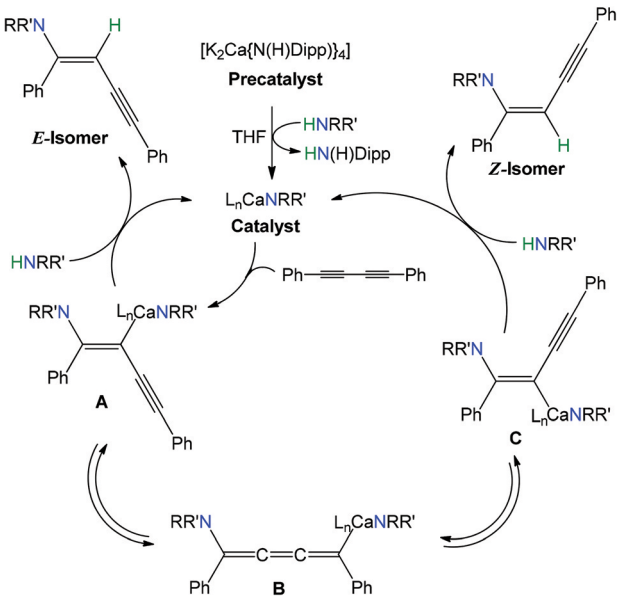
In these studies we used again the approved catalyst and varied the amine. The use of secondary amines guarantees that the rather complex cyclization reactions are suppressed. *N*-Methyl-anilines were reacted with diphenylbutadiyne in the presence of catalytic amounts of $[K_2Ca\{N(H)Dipp\}_4]$. In a standard procedure, diphenylbutadiyne was dissolved in tetrahydrofuran (THF). At room temperature, an equimolar amount of *N*-methyl-aniline HN(Me)C_6H_4-4-R (R = H, Me, F) and 5 mol% of the catalyst were added. This solution was stirred for several hours at room temperature. Repeated NMR measurements showed the conversion of the amine and the formation of singly hydroaminated diphenylbutadiynes (R = H [**1a**], Me [**1b**], F [**1c**]) as a mixture of *E*- and *Z*-isomers according to eqn (1). After quantitative conversion the reaction mixture was hydrolyzed with distilled water. The aqueous solution was extracted with diethyl ether. The ether fractions were combined, dried with sodium sulfate and then the ether was removed yielding *E*/*Z*-isomer mixtures of the tertiary amines 1-(*N*-methyl-anilino)-1,4-diphenylbut-1-ene-3-yne with *E*/*Z* ratios of approximately 1 : 0.6 (**1a**), 1 : 1 (**1b**) and 1 : 0.9 (**1c**). Recrystallization from a solvent mixture of dichloromethane and pentane gave pure compounds; however, the different isomers exhibited rather similar solubility properties hampering a fractional crystallization under these conditions.



	yield	isomeric ratios	
R = H	(**1 a**), 92 %	*Z*-**1a** 39 %	*E*-**1a** 61 %
Me	(**1 b**), 49 %	*Z*-**1b** 49 %	*E*-**1b** 51 %
F	(**1 c**), 48 %	*Z*-**1c** 48 %	*E*-**1c** 52 %

(1)

We could show earlier[8a] that also the addition of bulky 2,6-diisopropylphenylamine to diphenylbutadiyne can be achieved with $[K_2Ca\{N(H)Dipp\}_4]$. In order to release steric pressure, at least one diisopropylanilide anion is exchanged by an *N*-methyl-anilide *via* a transamination reaction forming the catalytically active species (Scheme 1) yielding L_nCa-NRR′. L represents Lewis bases such as solvent molecules (thf), amines or amide anions. The Ca–N bond adds to a C≡C triple bond leading to intermediate **A**. The newly formed and very reactive Ca–C moiety metalates an amine finally yielding *E*-**1** and regenerating the catalyst. Even though the *E*-isomers represent the major product, significant amounts of the *Z*-isomers are observed. A 1,3-shift of the negative charge leads to the formation of cumulene **B** (which might also exist as a solvent-separated ion pair). From this isomer, the back reaction reforms isomer **A** whereas also the other isomer C can be obtained. Metalation of amine by **C** yields *Z*-**1**.



Scheme 1 Proposed catalytic cycle for the calcium-mediated hydroamination of diphenylbutadiyne (Ph = phenyl; R,R′ = methyl, aryl). Due to the fact that the exact composition of the catalytic species is unknown, the calcium catalyst is shown as [L_nCaNRR'] with L representing any Lewis base such as thf (solvent), amines and amides such as the anions NRR'^- and $N(H)Dipp^-$.

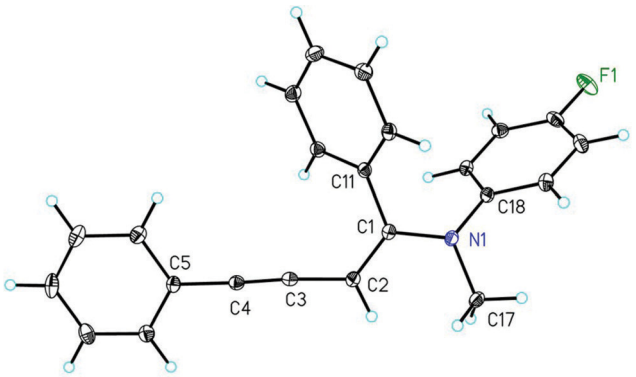


Fig. 1 Molecular structure and numbering scheme of *E*-**1c**. The ellipsoids represent a probability of 30%, H atoms are drawn with arbitrary radii. Selected structural parameters are listed in Table 1.

Table 1 Selected structural parameters (bond lengths [pm] and angles [°]) of the *E*-isomers *E*-**1a**, *E*-**1b**, and *E*-**1c**

	E-**1a**	*E*-**1b**	*E*-**1c**
N1–C17	146.78(16)	146.78(18)	146.76(13)
N1–C18	143.17(16)	143.10(17)	143.19(13)
N1–C1	139.99(15)	139.94(17)	139.97(13)
C1–C11	148.74(17)	149.09(18)	149.18(14)
C1–C2	135.33(17)	135.53(19)	135.77(15)
C2–C3	142.34(17)	142.29(19)	142.37(15)
C3–C4	120.27(18)	120.31(19)	120.40(15)
C4–C5	143.39(17)	143.38(19)	143.61(14)
C17–N1–C18	115.11(10)	115.06(11)	114.81(8)
C1–N1–C17	117.79(10)	117.88(11)	117.92(9)
C1–N1–C18	117.95(10)	119.37(11)	118.38(8)
N1–C1–C2	122.06(11)	121.07(12)	121.68(9)
N1–C1–C11	115.49(10)	115.49(11)	115.75(9)
C2–C1–C11	122.21(11)	123.22(12)	122.38(9)
C1–C2–C3	125.01(12)	126.78(13)	125.86(10)
C2–C3–C4	176.09(13)	173.87(14)	175.45(11)
C3–C4–C5	176.23(13)	177.59(14)	177.34(11)

The molecular structure and numbering scheme of *E*-(1,4-diphenylbut-1-ene-3-yne-1-yl)-(4-fluorophenyl)-methylamine (*E*-**1c**) is depicted in Fig. 1. The essential structural parameters of *E*-**1a**, *E*-**1b**, and *E*-**1c** are very similar and summarized in Table 1. The nitrogen atom N1 is in a nearly planar environment allowing conjugation of the lone pair with the but-1-ene-3-yne unit. The N1–C17 and N1–C18 bond lengths represent characteristic N–C values to sp^3 and sp^2 hybridized carbon atoms, respectively. The shorter N1–C1 bond lengths hint toward a slight conjugation with the alkene moieties. The π-system of the alkene fragments do not interact with the adjacent phenyl group. The C1═C2 bond (135.3 to 135.8 pm) is only slightly elongated compared to the expected value of a double bond between the sp^2 hybridized carbon atoms (134 pm).[9] The C3≡C4 bond reflects the characteristic value of an isolated triple bond.

Selected NMR data are summarized in Table 2. The numbering scheme for the carbon atoms is identical to the numbering of the X-ray structures discussed above. For the assignment, single crystals of the *E*-isomers were dissolved in an appropriate solvent and NMR experiments (H,H-COSY, HMBC and HSQC spectra) allowed an unambiguous assignment of these resonances. The NMR signals of the aryl groups are listed in the Experimental section, an assignment to specific carbon atoms was not possible. Thereafter, a mixture of both isomers allowed us to also assign the resonances of the *Z*-isomers.

The hydrogen atoms at the C2 atoms clearly allow us to distinguish between the *E*- and *Z*-isomer because the resonances of the *E*-isomers are shifted toward a lower field by approx. 0.5 ppm. A comparable effect, albeit smaller, is also observed for the *N*-bound methyl groups. In the $^{13}C\{^1H\}$ NMR spectra only small differences of the chemical shifts of the isomers can be found.

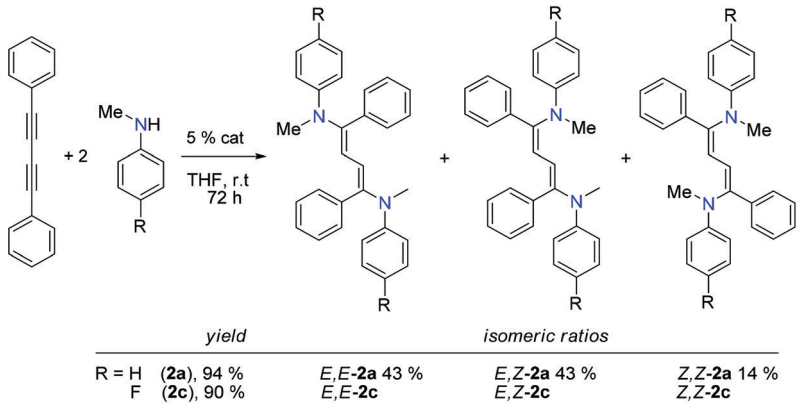
Doubly hydroaminated diphenylbutadiyne

The reaction of diphenylbutadiyne with a twofold stoichiometric amount of *N*-methyl-aniline (R = H) yielded after three days an *E*/*Z*-isomeric mixture of 1,4-di(*N*-methylanilino)-1,4-diphenylbuta-1,3-diene (**2a**) according to eqn (2). Again, the conversion was controlled by NMR spectroscopy measurements as depicted in Fig. 2. These NMR studies showed that the formation of the *E*-isomer is favored but again *cis*- and *trans*-addition was observed for the second hydroamination step, yielding *E*,*Z*- and *E*,*E*-1,4-di(*N*-methylanilino)-1,4-diphenylbuta-1,3-diene as the major components. The *E*,*E*- and *Z*,*Z*-isomers form with a ratio of 3 : 1. This is in agreement with the formation of the singly hydroaminated compounds *E*-**1a** and *Z*-**1a** where the *E*-isomer also represents the favored product. A complete conversion was not achieved under these reaction conditions. A final NMR experiment after approx. one month still contained singly hydroaminated **1a**.

The yields of doubly hydroamination products **2a** and **2c** were determined approx. after one month (eqn (2)) with minor amounts of the mono-hydroamination products **1a** and **1c**, respectively, still present. The ratio of the isomers of **2a** was determined by the integration of the ^1H NMR spectrum. For **2c** one major component was observed in the NMR spectra accompanied by resonances of very weak intensity (see the ESI†); therefore a reliable assignment was not possible in the ^1H NMR spectrum.

The time-dependent conversion of the singly hydroaminated diphenylbutadiyne **1a** to the doubly hydroaminated derivative **2a** is depicted in Fig. 3. The s-block metal-mediated hydroamination of the second CC triple bond of diphenylbutadiyne is significantly slower than the first hydroamination process, allowing the isolation of pure mono-hydroamination product **1a**. However, a mono-hydroaminated product was still present after several days and weeks. Thus, the reaction solution showed a mixture of 10% of *Z*-**1a** and 20% of *E*-**1a** as well as 30% of *E*,*E*-**2a**, 30% of *E*,*Z*-**2a** and 10% of *Z*,*Z*-**2a** after 72 hours.

The bulkier *N*-methyl-*p*-toluidine (R = Me) reacted only once regardless of the applied stoichiometry giving exclusively the



(2)

singly hydroaminated product **1b**. In contrast to this inhibition by a *para*-methyl substituent, the hydroamination of diphenylbutadiyne with *N*-methyl-*para*-fluoroaniline (R = F) showed that the second hydroamination step also occurred readily leading to *E*/*Z*-mixtures of 1,4-di(*N*-methyl-*para*-fluoroanilino)-1,4-diphenylbuta-1,3-diene (**2c**). The reaction of 1-(*N*-methylanilino)-1,4-diphenylbut-1-ene-3-yne (**1a**) with *N*-methyl-*para*-fluoroaniline led to the formation of the asymmetric 1,4-hydroaminated butadiene derivative **3**. Due to the lack of formation of symmetric **2a** and **2c** equilibrium with amination–deamination pathways can be excluded. In contrast to these findings *N*-methyl-toluidine again showed no tendency to react with the second C≡C triple bond of **1a** under these reaction conditions.

The centrosymmetric molecular structures of the doubly hydroaminated isomers *E*,*E*-**2a** and *Z*,*Z*-**2c** are displayed in Fig. 4 and 5. The asymmetric derivative **3** crystallized as a *Z*,*Z*-isomer in the centrosymmetric monoclinic space group $P2_1/c$ with the center of symmetry on the butadiene unit leading to 1 : 1 disordering of the 4-fluorophenyl and the *N*-bound unsubstituted phenyl groups. In Fig. 6, the C–F and C–H bonds to the disordered atoms with occupancy factors of 50% are shown as broken lines; only one orientation of this molecule is depicted. Due to the fact that the influence of the *para*-positioned substituents on the structure of the central moieties is negligible in the singly hydroaminated derivatives **1**, the structural parameters are reliable and are included in our discussions. Selected structural data are summarized in Table 3.

The central butadiene units resemble characteristic bond lengths of C–C single and C=C double bonds without significant charge delocalization. In agreement with this interpretation, the C1–C10 bond lengths to the phenyl groups resemble characteristic single bond values between sp^2 hybridized carbon atoms.[9] Due to the crystallographic inversion symmetry the buta-1,3-diene units are strictly planar. According to the VSEPR concept multiple bonds are more demanding than single bonds and therefore, they require more space leading to decreased N1–C1–C11 bond angles.

In the *E*-isomeric mono-hydroamination products **1a** to **1c**, the N–C bond to the butadiene fragment is shorter than the

Table 2 Selected NMR data of the singly hydroaminated diphenylbutadiyne. The numbering scheme is identical to the molecular structures and can be seen in Fig. 1

	E-**1a**	*E*-**1a**	*Z*-**1a**	*E*-**1b**	*Z*-**1b**	*E*-**1c**	*Z*-**1c**
Solvent	DMSO	[D_8]THF	[D_8]THF	[D_8]THF	[D_8]THF	CD_2Cl_2	CD_2Cl_2
^{1}H							
C2–H	5.96	5.83	5.28	5.69	5.17	5.75	5.21
C17–H	3.34	3.40	3.25	3.42	3.26	3.40	3.23
$^{13}C\{^1H\}$							
C1	155.1	155.9	158.2	156.2	158.2	157.9	160.5
C2	99.9	100.3	90.6	88.8	87.5	88.3	88.9
C3	97.4	98.4	90.8[a]	90.6[a]	90.9[a]	99.1	97.9
C4	88.3	88.6	91.1[a]	91.1[a]	90.1[a]	90.5	90.4
C11	137.6	139.3	137.7	139.6	137.2	137.1	138.8
C17	39.4	39.5	41.5	40.0	42.2	41.6	39.7
C18	147.0	148.3	149.2	146.7	146.1	144.6	145.1

[a] Assignment uncertain.

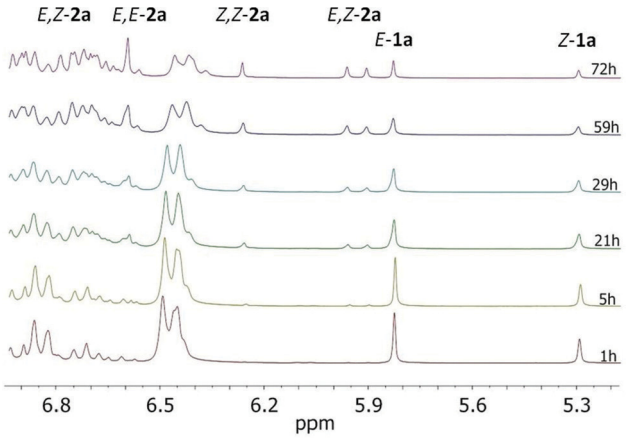


Fig. 2 NMR spectroscopic monitoring of the second hydroamination of an *E*/*Z*-mixture of **1a** in the presence of catalytic amounts of $[K_2Ca\{N(H)Dipp\}_4]$ (400 MHz, r.t., $[D_8]$THF). The progress of the second hydroamination step can be elucidated from the resonances of the butadiene units in the region between δ = 5.3 and 7.0 ppm. The spectra were recorded after 1 h, 5 h, 21 h, 29 h, 59 h, and 72 h (from bottom to top) after mixing of the substrates. In the bottom spectrum *E*-**1a** (δ = 5.82 ppm) and *Z*-**1a** (δ = 5.28 ppm) are the major components; after 72 h, these compounds together with the doubly hydroaminated diphenylbutadiynes *E*,*E*-**2a** (δ = 6.59 ppm), *E*,*Z*-**2a** (δ = 5.93 and 6.7 ppm), and *Z*,*Z*-**2a** (δ = 6.26 ppm) are observed.

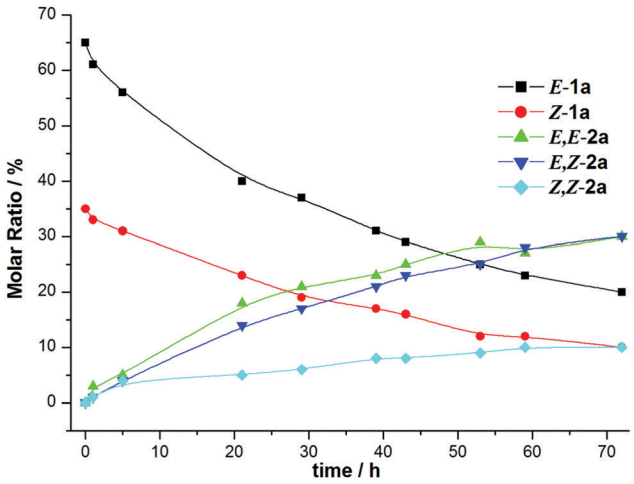


Fig. 3 Time-dependent conversion of the singly hydroaminated compounds *E*-**1a** and *Z*-**1a** to the doubly hydroaminated isomer mixture **2a** in the presence of 5 mol% of catalytically active $[K_2Ca\{N(H)Dipp\}_4]$ in THF at room temperature. Due to the fact that no side-products formed during this s-block metal-mediated hydroamination all compounds add up to 100%.

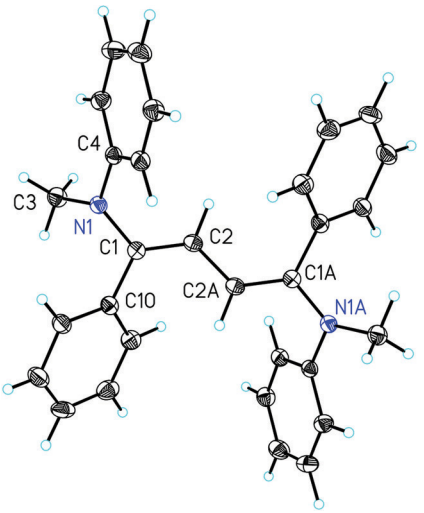


Fig. 4 Molecular structure and numbering scheme of centrosymmetric *E*,*E*-**2a**. Symmetry-related atoms are marked with the letter "A". The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected structural parameters are listed in Table 3.

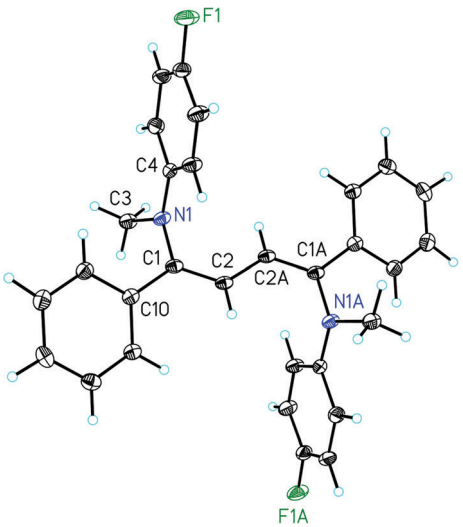


Fig. 5 Molecular structure and numbering scheme of centrosymmetric *Z*,*Z*-**2c**. Symmetry-related atoms are marked with the letter "A". The ellipsoids represent a probability of 30%, H atoms are drawn with arbitrary radii. Selected bond lengths and angles are summarized in Table 3.

bond to the aryl group. This trend is also realized in the doubly hydroaminated *E*,*E*-isomeric derivative. In the *Z*,*Z*-isomers **2c** and **3** a characteristic N1–C1 single bond is observed whereas a shortening of the N1–C4 bond to the adjacent aryl group resembles a slight interaction between the lone pair at N1 and the π-system of this aryl group. In *E*,*E*-isomeric **2a** the N1–C1 and N1–C4 bond lengths show very similar values with a smaller degree of charge delocalization. This finding verifies that the direction of the small contributions of π-interaction is dictated by the minimization of steric pressure within the molecules.

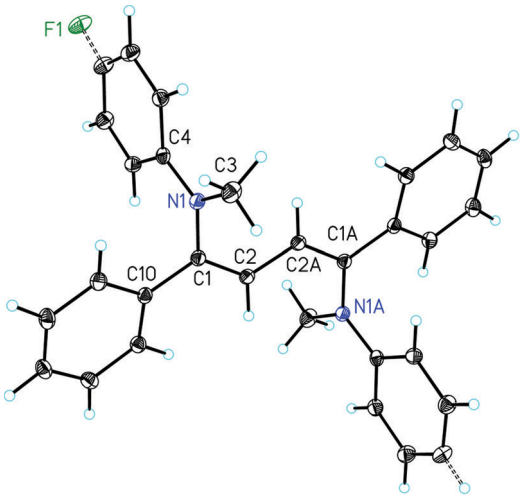


Fig. 6 Molecular structure and numbering scheme of *Z*,*Z*-**3**. Symmetry-related atoms are marked with the letter "A". Due to the centrosymmetry the fluorine and hydrogen atoms at C7 (the respective bonds are depicted as broken lines) is disordered with a 1 : 1 ratio, only one orientation is depicted in this figure (see text). The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii.

Table 3 Selected structural parameters (bond lengths [pm] and angles [°]) of the doubly hydroaminated diphenylbutadiyne

	E,*E*-**2a**	*Z*,*Z*-**2c**	*Z*,*Z*-**3**
N1–C4	141.9(3)	139.5(3)	139.2(3)
N1–C3	146.2(3)	146.0(3)	145.7(3)
N1–C1	141.4(3)	143.1(3)	142.9(2)
C1–C10	148.3(4)	147.7(4)	148.1(3)
C1–C2	136.0(4)	135.1(4)	135.1(3)
C2–C2A	143.8(5)	143.8(5)	144.3(4)
C3–N1–C4	116.9(2)	119.0(2)	119.8(2)
C1–N1–C3	117.6(2)	117.0(2)	118.6(2)
C1–N1–C4	120.8(2)	121.5(2)	121.5(2)
C2–C1–C10	123.8(2)	122.0(2)	122.4(2)
N1–C1–C10	115.1(2)	117.2(2)	117.5(2)
N1–C1–C2	121.1(2)	120.8(2)	119.8(2)
C1–C2–C2a	126.6(3)	125.5(3)	125.0(2)

Conclusion

The proven precatalyst $[K_2Ca\{N(H)Dipp\}_4]$ was employed to study the hydroamination of diphenylbutadiyne with secondary *N*-methyl-anilines in tetrahydrofuran at room temperature. After approximately 6 h a nearly complete conversion with a catalyst loading of 5 mol% led to singly hydroaminated butadiyne. Diverse *para*-substituents such as H, Me and F were tested and yielded the desired hydroamination products (*N*-methyl)-(*N*-aryl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine of the type [Ph–C≡C–CH=(Ph)C]N(Me)(C_6H_4-4-R) with R = H (**1a**), Me (**1b**) and F (**1c**). This hydroamination was regioselective; however, both stereoisomers with *E*- and *Z*-arrangements at the C=C double bond were formed.

The second hydroamination step of the other C≡C triple bond requires much longer time under similar reaction conditions. After three days mixtures of singly and doubly hydroaminated diphenylbutadiyne were obtained when *N*-methylaniline and *N*-methyl-4-fluoroaniline were employed. In contrast to this finding, no significant amount of doubly hydroaminated diphenylbutadiyne was observed in the NMR spectra for the hydroamination with *N*-methyl-4-tolylamine. Again, the catalytic hydroamination gave regioselectively 1,4-diphenyl-1,4-bis(*N*-methylanilino)buta-1,3-diene [R = H (**2a**) and F (**2c**)] but a mixture of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-stereoisomers was obtained. The extremely decelerated second hydroamination allowed the isolation of pure singly hydroaminated diphenylbutadiyne. The catalytic hydroamination of **1a** with *N*-methyl-4-fluoroaniline yielded exclusively the mixed doubly hydroaminated product **3** as a stereoisomeric mixture. The absence of **2a** and **2c** verifies that amination–deamination equilibrium can be excluded.

The X-ray structures of *E*-isomeric **1** suggest that the lone pair of the nitrogen atoms show only a very small interaction with the π-systems of the adjacent C=C double bonds whereas no delocalization into the *N*-bound aryl groups can be substantiated. The second amino group enhances steric strain and in *Z*,*Z*-isomeric **2c** and **3** the lone pairs of the nitrogen atoms slightly interact with the π-systems of the *N*-bound aryl groups. This observation suggests that steric reasons might account for the significantly slower second hydroamination step.

Experimental

General remarks

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. The solvent was dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. The yields given are not optimized. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AC 400 and AC 600 spectrometers. Chemical shifts are reported in parts per million relative to $SiMe_4$ as an external standard. The residual signals of the deuterated solvents [D_8]THF and CD_2Cl_2 were used as internal standards. The solvent-free and recrystallized precatalyst $[K_2Ca\{N(H)Dipp\}_4]$ was prepared according to a literature procedure.[8] A specific amount of this compound was dissolved in anhydrous THF and aliquots of this solution were added to the reaction mixtures. This procedure allowed us to easily add definite amounts of the precatalyst to the substrates under strictly anaerobic conditions. All substrates were purchased from Sigma Aldrich, Merck or Alfa Aesar and used without further purification. The isomeric ratios are discussed in the text and are given underneath the reaction equations.

(*N*-Methyl)-1,4-diphenylbut-1-ene-3-yne-1-ylaniline (1a). To a solution of diphenylbutadiyne (0.25 g, 1.23 mmol) in 20 ml of THF, *N*-methylaniline (0.13 g, 1.23 mmol) and 5 mol% of the calciate precatalyst $[K_2Ca\{N(H)Dipp\}_4]$ were added and stirred

for 6 hours at r.t. A standard workup procedure including hydrolysis with 17 ml of distilled water, extraction with diethyl ether, drying with sodium sulfate and recrystallization in pentane at 5 °C yielded colorless crystals from a yellow mother liquor (0.35 g, 1.13 mmol, 92%). M.p. 118 °C. Elemental analysis ($C_{23}H_{19}N$, 309.39): calc.: C 89.28, H 6.19, N 4.53; found: C 88.84, H 6.26, N 4.47. MS [EI, *m*/*z* (%)]: 309 (90) [M], 202 (15) [diyne], 146 (15), 118 (100) [$PhNC_2H_3$], 91 (10) [N-Ph], 77 (45) [Ph]. IR 3078 w, 3055 w, 3032 w, 2998.54 w, 2958 w, 2889 w, 2815 w, 2188 w, 1596 s, 1578 s, 1560 w, 1549 w, 1487 s, 1471 m, 1422 w, 1385 m, 1095 m, 1026 m, 1007 m, 917 m, 751 vs, 694 vs, 588 w, 521 m, 493 m, 407 w.

***E*-Isomer**: ^{1}H NMR (400 MHz, DMSO): δ 7.46 (m, 2H, Ar–*H*), 7.36 (m, 3H, Ar–*H*), 7.30 (m, 3H, Ar–*H*), 7.15 (m, 4H, Ar–*H*), 6.78 (d, $^3J_{H,H}$ = 8.1 Hz, 2H,), 6.72 (t, $^3J_{H,H}$ = 7.2 Hz, 1H, C21*H*), 5.96 (s, 1H, C2*H*), 3.34 (s, 3H, C17*H*). $^{13}C\{^1H\}$ NMR (DMSO, *E*-isomer): δ 155.1 (*C*1), 147.0 (*C*18), 137.61 (*C*11), 130.9, 129.2, 128.8, 128.7, 128.6, 128.3, 127, 123.1, 118.6, 116.1, 99.9 (*C*2), 97.4 (*C*3), 88.3 (*C*4), 39.4 (*C*17).

Mixture of *E*- and *Z*-isomers (approx. 6 : 4): ^{1}H NMR (400 MHz, [D_8]THF): δ 7.60 (d, $^3J_{H,H}$ = 7.1 Hz, Ar–*H*), 7.47 (m, Ar–*H*), 7.19 (m, Ar–*H*), 7.01 (d, *J* = 7.8 Hz, Ar–*H*), 6.85 (d, $J_{H,H}$ = 8.2 Hz, Ar–*H*), 6.71 (t, *J* = 7.3 Hz, Ar–*H*), 5.83 (s, C2*H*, *E*), 5.28 (s, C2*H*, Z), 3.40 (s, H_3, *E*), 3.25 (s, CH_3, *Z*). $^{13}C\{^1H\}$ NMR (101 MHz, [D_8]THF): δ 158.2 (*C*1, *Z*), 155.9 (*C*1, *E*), 149.2 (*C*18, *Z*), 148.3 (*C*18, *E*), 139.3 (*C*11, *E*), 137.7 (*C*11, *Z*), 131.8, 131.1, 130.8, 129.5, 129.3, 129.2, 129.1, 128.9, 128.7, 128.3, 128.2, 127.9, 127.3, 125.9, 124.9, 124.3, 123.4, 119.4, 117.2, 100.3 (*C*2, *E*), 98.4(*C*3, *E*), 91.1 (*C*4, *Z*), 90.8 (*C*3, *Z*), 90.6 (*C*2, *Z*), 88.6 (*C*4, *E*), 41.5 (*C*17, *E*), 39.5 (*C*17, *E*).

(*N*-Methyl)-(*N*-4-tolyl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine (1b). To a solution of diphenylbutadiyne (0.25 g, 1.23 mmol) in THF (17 ml), *N*-methyl-*p*-toluidine (0.149 g, 1.23 mmol) and 5 mol% of the calciate [K_2Ca{N(H)Dipp}$_4$] were added and stirred for 7 hours at r.t. Hydrolysis with 15 ml of distilled water, extraction with diethyl ether, drying with sodium sulfate and recrystallization in pentane at 5 °C yielded colorless crystals in a yellow mother liquor (0.35 g, 1.08 mmol, 88%). M.p. 120 °C. Elemental analysis ($C_{24}H_{21}N$, 323.42): calc.: C 89.12, H 6.54, N 4.33; found: C 88.86, H 6.64, N 4.49. MS [EI, *m*/*z* (%)]: 323 (100) [M], 202 (15) [Ph_2C_4], 146 (15), 118 (100) [$PhNC_2H_3$], 91 (10) [N-Ph], 77 (20) [Ph], 43 (60). IR: 3064 w, 3030 w, 2899 w, 2876 w, 2857 w, 2821 w, 2186 w, 2170 w, 1598 s, 1565 m, 1513 s, 1549 w, 1486 m, 1469 m, 1444 m, 1360 s, 1105 s, 801 s, 762 s, 749 s, 704 s, 693 s, 523 m, 521 m, 503 m, 485 m, 474 w.

***E*-Isomer**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65–6.83 (m, 14H), 5.17 (s, 1H, C2*H*), 3.26 (s, 3H, C17*H*), 2.22 (s, 3H, C24*H*). ^{13}C NMR (101 MHz, CD2Cl2) δ 158.2 (*C*1, *E*), 146.1 (*C*18, *E*), 137.2(*C*11, *E*), 133.5, 130.7, 130.5, 129.7, 128.6, 128.5, 127.9, 127.1, 125.2, 124.9, 90.9 (*C*3, *E*), 90.1 (*C*4, *E*), 87.5 (*C*2, *E*), 42.2 (*C*17, *E*), 20.8 (*C*24, *E*).

Mixture of *E*- and *Z*-isomers (1 : 1): ^{1}H NMR (600 MHz, thf-d_8): δ 7.60–7.54 (m, 2H, Ar–*H*, *E*,*Z*), 7.44 (m, 2H, Ar–*H*, *E*,*Z*), 7.32–7.08 (m, 16H, Ar–*H*, *E*,*Z*), 6.92 (m, 6H, Ar–*H*, *E*,*Z*), 6.81–6.72 (m, 2H, Ar–*H*, *E*,*Z*), 5.69 (s, 1H, C2*H*, *Z*), 5.18 (s, 1H, C2*H*, *E*), 3.42 (s, 3H, C17*H*, *Z*), 3.22 (s, 3H, C17*H*, *E*), 2.19 (s, 3H, C24*H*, *Z*), 2.18 (s, 3H, C24*H*, *E*). $^{13}C\{^1H\}$ NMR (151 MHz, thf-d_8) δ 158.5 (*C*1, *E*), 156.2 (*C*1, Z), 146.7 (*C*18, *E*), 146.1 (*C*18, *Z*), 139.6 (*C*11, *Z*), 137.8 (*C*11, *E*), 133.3, 131.7, 131, 130.9, 129.7, 129.3, 129.1, 128.9, 128.8, 128.7, 128.7, 128.2, 128.1, 127.2, 126.1, 125.1, 124.9, 118.1, 98.7 (*C*2, *E*), 98 (*C*3, *E*), 91.1 (*C*4, *Z*), 90.6 (*C*3, *Z*), 89 (*C*4, *E*), 88.8 (*C*2, *Z*), 41.8 (*C*17, *E*), 40 (*C*17, *Z*), 20.6 (*C*24, *E*), 20.4 (*C*24, *Z*).

(*N*-Methyl)-(*N*-4-fluorophenyl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine (1c). To a solution of diphenylbutadiyne (0.15 g 0.74 mmol) in THF (12 ml), 4-fluoro-*N*-methylaniline (0.092 g, 0.74 mmol) and 5 mol% of the calciate catalyst [K_2Ca{N(H)-Dipp}$_4$] were added and stirred for six hours at r.t. A standard workup procedure including hydrolysis with 10 ml of distilled water, extraction with diethyl ether, drying with sodium sulfate and recrystallization in the diffusion method (dichloromethane/pentane) at 5 °C yields colorless crystals in yellow solution (0.190 g 0.58 mmol, 78%). M.p. 121 °C. Elemental analysis ($C_{30}H_{27}N_2F$, 434.22): calc.: C 84.38, H 5.54, N 4.28, F 5.80; found: C 84.12, H 5.58, N 4.45. MS [EI, *m*/*z* (%)]: 327 (100) [M], 202 (50) [diyne], 189 (30), 118 (100) [$PhNC_2H_3$], 95 (60), 77 (90) [Ph]. IR: 3052 w, 3028 w, 2919 w, 2849 w, 2184 w, 1580 w, 1560 m, 1504 s, 1486 s, 1469 m, 1441 m, 1360 m, 1486 m, 1222 s, 1108 m, 1023 w, 915 m, 795 s, 754 s, 688 s, 535 m, 524 m, 523 m, 487 m, 474 w, 428 w.

Mixture of *E*- and *Z*-isomers: ^{1}H NMR (400 MHz, [D_8]THF): δ 7.59–7.54 (m, Ar–*H*), 7.48–7.42 (m, Ar–*H*), 7.33–7.09 (m, Ar–*H*), 7.04–6.98 (m, Ar–*H*), 6.92–6.81 (m, Ar–*H*), 5.75 (s, C2*H*, *E*), 5.21 (s, C2*H*, Z), 3.40 (s, CH_3, *E*), 3.23 (s, CH_3, *Z*). $^{13}C\{^1H\}$ NMR (101 MHz, [D_8]THF): δ 160.5 (*C*1, *Z*), 158.3 (d, $^1J_{C,F}$ = 24.3 Hz), 157.9 (*C*1, *E*), 156.1 (*C*22, *Z*), 155.6 (*C*22, *E*), 145.13 (d, $^4J_{C,F}$ = 2.6 Hz, *C*18, *Z*), 144.56 (d, $^4J_{C,F}$ = 2.1 Hz, *C*18, *E*), 138.8 (*C*11, *Z*), 137.1, 132, 131.3, 130.7, 130.5, 129.2, 128.8, 128.6, 128.5, 128.4, 128, 127.8, 127.6, 127, 126.4, 126.3, 125.6, 124.5, 122.5, 118.5, 118.5, 117.7, 115.7, 115.5, 115.3, 115.1, 99.1, 97.9, 90.5, 90.4, 88.9, 88.3, 41.6 (*C*17, *E*), 39.7 (*C*17, *Z*). ^{19}F NMR (188 MHz, THF): δ −123 (*Z*), −129.2 (*E*).

1,4-Diphenyl-1,4-bis(*N*-methylanilino)buta-1,3-diene (2a). Diphenylbutadiyne (0.25 g, 1.23 mmol) was dissolved in 17 ml of THF before *N*-methylaniline (0.26 g, 2.47 mmol) and 5 mol % of calciate [K_2Ca{N(H)Dipp}$_4$] were added and stirred for three days at r.t. The standard workup procedure included hydrolysis with 15 ml of distilled water, extraction with diethyl ether, drying with sodium sulfate and fractional recrystallization from dichloromethane and pentane at 5 °C yielding 0.45 g of colorless crystals from a yellow solution. The crystal fraction contained also minor amounts of **1a**. M.p. 121 °C. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.62 (d, *J* = 7.2 Hz, Ar–*H*), 7.48 (m, Ar–*H*), 7.42 (d, $J_{H,H}$ = 7.7 Hz, Ar–*H*), 7.38–7.30 (m, Ar–*H*), 7.31–7.24 (m, Ar–*H*), 7.25–7.21 (m, Ar–*H*), 7.21–7.12 (m, Ar–*H*), 7.09 (t, $J_{H,H}$ = 7.9 Hz, Ar–*H*), 7.02 (d, *J* = 7.8 Hz, Ar–*H*), 6.96–6.90 (m, Ar–*H*), 6.89 (d, $J_{H,H}$ = 8.2 Hz, Ar–*H*), 6.84–6.75 (m, Ar–*H*), 6.72 (m, Ar–*H*), 6.70–6.65 (m, Ar–*H*), 6.61 (d, $J_{H,H}$ = 8.1 Hz, Ar–*H*), 6.59 (s, C2*H*, C2A*H*, *Z*–*Z*), 6.24 (s, C2*H*, C2A*H*, *E*–*E*), 5.94 (d, $^3J_{H,H}$ = 11.3 Hz, C2*H*, C2A*H*, *E*–*Z*, *Z*–*E*), 5.79 (s, C2*H*, *E*), 5.28 (s, C2*H*, *Z*), 3.43 (s, C17H_3, *E*), 3.30 (s, C17H_3, *Z*), 3.24 (s, CH_3, *E*–*E*),

3.13 (s, CH_3, *Z*–*Z*), 3.11 (s, CH_3, *E*–*Z*, *Z*–*E*). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 157. (*C*1, *Z*), 155.6(*C*1, *E*), 150.51 (*C*18, *Z*), 149.37 (*C*18, *E*), 148.9, 148.8, 148.7, 148.6, 147.9, 146, 145.4, 139.6, 139.1, 138.8, 138.6, 138.1, 137.8, 137.1, 131.4, 130.8, 130.7, 130.5, 130.1, 129.3, 129.3, 129.1, 128.9, 128.9, 128.9, 128.9, 128.8, 128.7, 128.7, 128.5, 128.4, 128.4, 128.2, 128, 127.6, 127.2, 127.1, 127, 125.9, 125.1, 124.4, 124.1, 123.8, 123.3, 122.7, 122, 121.1, 119.7, 119.2, 119.1, 117.6, 117, 116.8, 116.8, 113.9, 113.1, 112.6, 110.6, 99.9 (*C*2, *E*), 97.9 (*C*3, *E*) 90.62 (*C*2, *Z*), 89.3 (*C*2, *C*3, *Z*), 88.3 (*C*4, *E*), 41.9 (*C*17, *Z*), 41.4 (*C*3,*C*3A, *Z*–*Z*), 40.4 (*C*3,*C*3A, *Z*–*E*, *E*–*Z*), 39.7 (*C*17-*E*), 39.2 (*C*3, *E*,*E*). Elemental analysis ($C_{30}H_{28}N_2$, 323.42): calc.: C 86.50, H 6.78, N 6.72; found: C 86.52, H 6.48, N 7.00. MS [EI, *m*/*z* (%)]: 417 (23) [M+], 417 (78) [M], 309 (95) [M − L], 202 (35) [diyne], 118 (90) [$PhNC_2H_3$], 91 (35) [N-Ph], 77 (100) [Ph]. IR 3027 w, 2962 w, 2901 w, 2189 w, 1598 s, 1580 s, 1561 vs, 1487 m, 1471 s, 1445 s,

Table 4 Crystal data and refinement details for the X-ray structure determinations of compounds **1a–1c** and **2a–3**

Compound	*E*-**1a**	*E*-**1b**	*E*-**1c**
Formula	$C_{23}H_{19}N$	$C_{24}H_{21}N$	$C_{23}H_{18}FN$
f_w (g mol^{-1})	309.39	323.42	327.38
T/°C	−140(2)	−140(2)	−140(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	7.2645(2)	7.4316(1)	7.2846(1)
b/Å	22.7706(5)	23.6631(7)	23.2679(5)
c/Å	10.5374(2)	10.6845(3)	10.5794(2)
α/°	90	90	90
β/°	97.257(1)	100.375(2)	98.835(1)
γ/°	90	90	90
V/Å^3	1729.10(7)	1848.20(8)	1771.90(6)
Z	4	4	4
ρ (g cm^{-3})	1.188	1.162	1.227
μ (cm^{-1})	0.68	0.67	0.78
Measured data	11 309	10 544	12 883
Data with $I > 2\sigma(I)$	3367	3444	3744
Unique data (R_{int})	3947/0.0301	4224/0.0313	4032/0.0211
wR_2 (all data, on F^2)[a]	0.0996	0.1079	0.0912
R_1 ($I > 2\sigma(I)$)[a]	0.0432	0.0468	0.0385
S[b]	1.064	1.069	1.048
Res. dens./e Å^{-3}	0.195/−0.166	0.263/−0.183	0.234/−0.183
Absorpt method	Multi-scan	Multi-scan	Multi-scan
Absorpt corr $T_{min/max}$	0.6322/0.7456	0.6553/0.7456	0.7006/0.7456
CCDC no.	1426897	1426898	1426899
Compound	*E*,*E*-**2a**	*Z*,*Z*-**2c**	*Z*,*Z*-**3**
Formula	$C_{30}H_{28}N_2$	$C_{30}H_{26}F_2N_2$	$C_{30}H_{27}FN_2$
f_w (g mol^{-1})	416.54	452.53	434.54
T/°C	−140(2)	−140(2)	−140(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	10.5309(15)	11.0689(3)	11.7393(4)
b/Å	11.255(2)	12.6418(4)	8.3583(3)
c/Å	10.6349(17)	8.3768(2)	11.9106(4)
α/°	90	90	90
β/°	113.94(1)	102.224(2)	100.576(2)
γ/°	90.00	90	90
V/Å^3	1152.1(3)	1145.60(6)	1148.82(7)
Z	2	2	2
ρ (g cm^{-3})	1.201	1.312	1.256
μ (cm^{-1})	0.7	0.88	0.79
Measured data	7660	6189	7762
Data with $I > 2\sigma(I)$	1700	1963	2346
Unique data (R_{int})	2507/0.0594	2173/0.0364	2618/0.0360
wR_2 (all data, on F^2)[a]	0.1796	0.1838	0.1824
R_1 ($I > 2\sigma(I)$)[a]	0.0791	0.0648	0.0671
S[b]	1.135	1.153	1.159
Res. dens./e Å^{-3}	0.214/−0.309	0.295/−0.241	0.378/−0.241
Absorpt method	Multi-scan	Multi-scan	Multi-scan
Absorpt corr $T_{min/max}$	0.5072/0.7456	0.5222/0.7456	0.6842/0.7456
CCDC no.	1426900	1426901	1426902

[a] Definition of the *R* indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2)]/3$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

1363 m, 1335 w, 1305 w, 1260 m, 1237 m, 1189 m, 1106 s, 1028 s, 766 m, 746 vs, 720 vs, 690 vs, 682 vs, 524 m, 499 m, 407 w.

1,4-Diphenyl-1,4-bis(*N*-methyl-4-fluoroanilino)buta-1,3-diene (2c). To a solution of diphenylbutadiyne (0.1 g, 0.49 mmol) in 12 ml of THF, *N*-methyl-4-fluoroaniline (0.12 g, 0.115 ml, 0.10 mmol) and 5 mol% of $[K_2Ca\{N(H)Dipp\}_4]$ were added and stirred for three days at r.t. Hydrolysis with 15 ml of distilled water, extraction with diethyl ether, drying with sodium sulfate and recrystallization from dichloromethane and pentane at 5 °C yielded colorless crystals in a yellow mother liquor (0.20 g, 0.44 mmol, 90%). M.p. 196–201 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.29–7.21 (m, 10H, Ar–*H*), 6.95–6.84 (m, 4H, Ar–*H*), 6.74–6.66 (m, 4H, Ar–*H*), 6.52 (s, 2H, C1*H*, C1A*H*), 3.26 (s, 6H, C9, C9A, C*H*3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 156.1 (d, $^1J_{C,F}$ = 235.0 Hz, *C*13, *C*13A), 146.1 (*C*2,*C*2A), 145.35 (d, $^4J_{C,F}$ = 1.8 Hz *C*10,*C*10A), 138.5 (*C*3,*C*3A), 128.9, 128.5, 127, 120.7, 115.7, 115.5, 114.7, 40 (*C*9, *C*9A). ^{19}F NMR (188 MHz, CD_2Cl_2): δ −129.5. Elemental analysis ($C_{30}H_{26}N_2F_2$, 452.53): calc.: C 79.62, H 5.79, N 6.19; found: C78.89, H 5.72, N 5.98. MS [EI, *m*/*z* (%)]: 453 (40) $[M]^+$, 452 (80) [M], 328 (30) $[M - L]^+$, 327 (95) [M − L], 202 (25) [diyne], 118 (100) $[PhNC_2H_3]$, 77 (20) [Ph]. IR: 3051 w, 2942 w, 2909 w, 2894 w, 2821 w, 2186 w, 2186 w, 1946 w, 1840 w, 1582 m, 1561 m, 1502 vs, 1441 m, 1349 s, 1295 m, 1218 s, 1094 s, 991 m, 811 s, 787 vs, 635 m, 600 s, 504 s, 472 w.

1,4-Diphenyl-1-(*N*-methyl-anilino)-4-(*N*-methyl-4-fluoroanilino)buta-1,3-diene (3). To a solution of *N*-(1,4-diphenylbut-1-en-3-yne-1yl)-*N*-methylaniline (**1**) (0.120 g, 0.38 mmol) in 15 ml of THF, 4-fluoro-*N*-methylaniline (0.048 g, 0.38 mmol) and 5 mol% of the catalyst $[K_2Ca\{N(H)Dipp\}_4]$ were added three times every 4 days and stirred for 12 days at r.t. A standard workup procedure including hydrolysis with 20 ml of distilled water, extraction with diethyl ether, drying with sodium sulfate and recrystallization from dichloromethane/pentane at 5 °C yields colorless crystals from a yellow solution (0.08 g, 0.18 mmol, 47%). M.p. 136–137 °C. ^{1}H NMR (600 MHz, C_6D_6): δ 7.33–7.23 (m, 3H, Ar–*H*), 7.19–7.16 (m, 6H, Ar–*H*), 7.03–6.90 (m, 8H, Ar–*H*), 6.82 (m, 4H, Ar–*H*), 6.75 (m, 1H, Ar–*H*), 6.65 (s, 2H, C2*H*, C2A*H*), 6.57–6.49 (m, 2H, Ar–*H*), 2.93 (s, 3H, C3*H*), 2.85 (s, 3H, C3A*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ 156.47 (d, $^1J_{C,\ F}$ = 235.8 Hz, *C*7), 148.8, 146 (d, ^4J = 26.7 Hz, *C*4), 145.2, 138.6, 138.5. 129.5, 128.9, 128.9, 128.4, 127.55, 126.97, 127, 120.5, 120.3, 118.2, 115.9, 115.8, 115, 114.9, 114.2, 39.3, 38.9. ^{19}F NMR (188 MHz, C_6D_6): δ −120.9 (*E*,*Z* isomer), −128 (*E*,*E* isomer), −129.6 (*Z*,*E* isomer). Elemental analysis ($C_{30}H_{27}N_2F$, 434.22): calc.: C 82.92, H 6.26, N 6.45, F 4.37; found: C83.25, H 5.72, N 6.40. MS [EI, *m*/*z* (%)]: 434 (100) [M], 316 (40), 309 (50) [M − L], 293 (40), 217 (75), 198 (55), 180 (40), 118 (65) $[PhNC_2H_3]$, 77 (40) [Ph]. IR 3030 w, 2959 w, 2876 w, 2814 w, 2184 m, 1582 m, 1558 m, 1490 s, 1439 m, 1333 m, 1321 m, 1260 m, 1165 m, 1113 s, 1008 m, 874 m, 776 s, 758 vs, 693 vs, 582 m, 516 m, 498 m, 468 s.

X-Ray structure determinations

The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[10–12] The structure was solved by direct methods (SHELXS)[13] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97).[13] All non-disordered hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.[13] Crystallographic data as well as structure solution and refinement details are summarized in Table 4. The programs XP (SIEMENS Analytical X-ray Instruments, Inc.)[14] and POV-Ray[15] were used for structure representations.

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Inorganic Chemistry

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Calcium-Mediated Catalytic Synthesis of 1-(Diorganylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes

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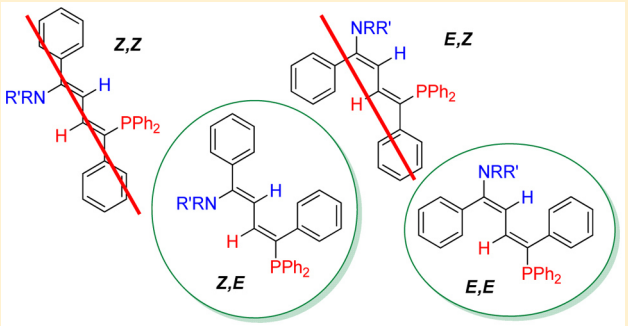
Supporting Information

ABSTRACT: The hydroamination of diphenylbutadiyne with 1 equiv of the secondary amines HNRR′ (R/R′ = Ph/Ph, Ph/Me, and pTol/Me) in the presence of catalytic amounts of the tetrakis(amino)calciate $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) yields the corresponding 1-(diorganylamino)-1,4-diphenylbut-1-ene-3-ynes as a mixture of *E*/*Z* isomers. These tertiary alkenylamines react with diphenylphosphane to form RR′N−C(Ph)═CH−CH═C(Ph)−PPh_2 [R/R′ = Ph/Ph (**1**), Ph/Me (**2**), and pTol/Me (**3**)] in the presence of catalytic amounts of $[(THF)_4Ca(PPh_2)_2]$ or of the same calciate $K_2[Ca\{N(H)Dipp\}_4]$. Whereas the hydroamination is regio- (amino group in 1-position) but not stereoselective (formation of *E* and *Z* isomers), this second hydrofunctionalization step is regio- (phosphanyl group in 4-position) and stereoselective (only *E* isomers are formed), finally leading to mixtures of (*E*,*E*)- and (*Z*,*E*)-1-(diorganylamino)-1,4-diphenyl-4-(diphenylphosphanyl)-buta-1,3-dienes.



INTRODUCTION

Hydrofunctionalization (hydroelementation, hydropentelation) resembles an atom-economic addition of H−E bonds [E being the penteles N (hydroamination) and P (hydrophosphanylation)] to alkenes and alkynes; however, several challenges must be solved. Hydroamination and hydrophosphanylation represent only slightly exothermic reactions that are entropically disfavored. In addition, the approach of a Lewis base (primary or secondary amine and phosphane) to an electron-rich C═C and C≡C multiple bond is disadvantageous and requires an effective catalyst to overcome the electrostatic repulsion. Several strategies have been developed, and recently, alkaline earth metal-mediated hydropentelation catalysis has gained significant interest.[1−3] Calcium-based catalysts are especially attractive because these alkaline earth metals are globally abundant, inexpensive, easily available, and nontoxic.

Intramolecular hydroamination of alkenes eliminates the entropic disadvantage and eases the addition of H−N bonds to C═C bonds. Calcium-based catalysts are able to catalyze this reaction, yielding azacycloalkanes.[4] Intermolecular hydroamination is achieved only with activated alkenes[5] and is much easier with C≡C bonds, requiring more reactive calcium-based catalysts correlated with the risk of also promoting undesired side reactions.[6] The reactivity of a calcium amide can be enhanced by the formation of a calciate. The catalyst should be coligand-free in order to avoid desolvation of the isolated crystalline compound due to uncontrolled loss of ligated Lewis bases such as ethers. This fact is important to allow an accurate ratio of catalyst to substrate. The heterobimetallic compound $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) with a tetracoordinate calcium atom fulfills these requirements and hence represents an approved catalytically active calciate because this ether-free complex is soluble in ethereal solvents.[7]

The reaction pathway of primary amines H_2NR with butadiynes strongly depends on the reaction conditions and the *N*-bound substituent. Nevertheless, both N−H bonds are able to add to alkyne moieties, yielding either 2,5-substituted pyrroles at high reaction temperatures[8] or multicyclic imines at room temperature and prolonged reaction times.[7,8] Secondary amines can add only once; hence, cyclic products are avoided.[6,9] Thus, *N*-alkyl anilines add to one or both C≡C bonds of the butadiyne backbone, depending on the reaction time, the stoichiometry of the substrates, and the amount of calcium catalyst, yielding 1-aminobut-1-ene-3-yne or 1,4-diaminobuta-1,3-dienes, respectively. In contrast to this observation, secondary diphenylphosphane always adds twice to both C≡C bonds of the butadiyne unit in the presence of catalytic amounts of $[(THF)_4Ca(PPh_2)_2]$ (THF = tetrahydrofuran, Scheme 1).[10] Even a large excess of butadiyne leads to the formation of bis-phosphanylated compounds, and unreacted alkyne remains in the reaction mixture. The hydrophosphanylation of substituted butadiynes with diphenylphosphane yields primarily 1,4-bis(diphenylphosphanyl)-buta-1,3-dienes; however, other regioisomers such as 1,2-bis(diphenylphosphanyl)buta-1,3-dienes have also been observed. Neither the hydroamination nor the hydrophosphany-

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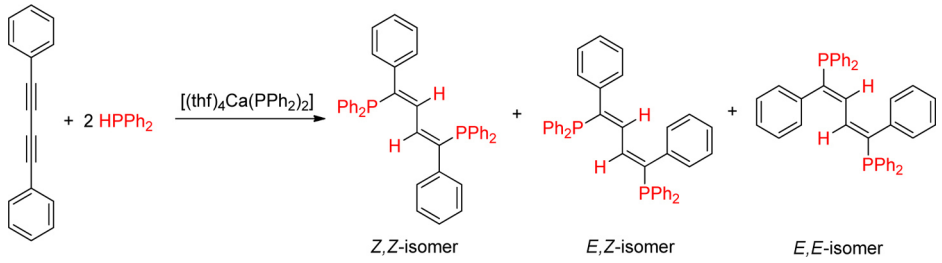
Scheme 1. Calcium-Mediated Hydrophosphanylation of Diphenylbutadiyne with Diphenylphosphane Yielding Isomeric Mixtures of 1,4-Bis(diphenylphosphanyl)buta-1,3-dienes



lation is stereoselective, but mixtures of *E* and *Z* isomers are formed.

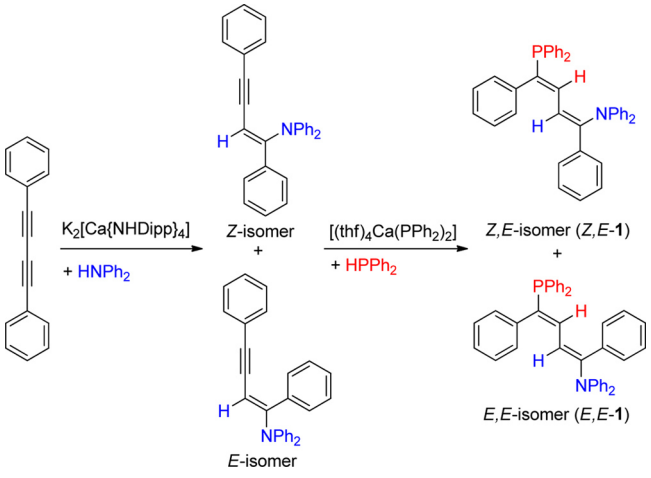
These findings suggest that the synthesis of substituted 1-amino-4-phosphanylbuta-1,3-dienes requires hydroamination as the initial step and hydrophosphanylation as a subsequent reaction. A further objective was the elucidation of the necessity to change the calcium-based catalyst from $K_2[Ca\{N(H)Dipp\}_4]$ for hydroamination to $[(THF)_4Ca(PPh_2)_2]$ for the following hydrophosphanylation. On the basis of the pK_a values of arylamines (approximately 31, depending on the substitution pattern), *N*-methyl-aniline (29.5), diphenylamine (25.0), and diphenylphosphane (22.9),[11] the calciate $K_2[Ca\{N(H)Dipp\}_4]$ is able to deprotonate secondary amines and diphenylphosphane, which is a precondition for the suitability of this calciate as a catalyst for hydropentelation reactions.

RESULTS AND DISCUSSION

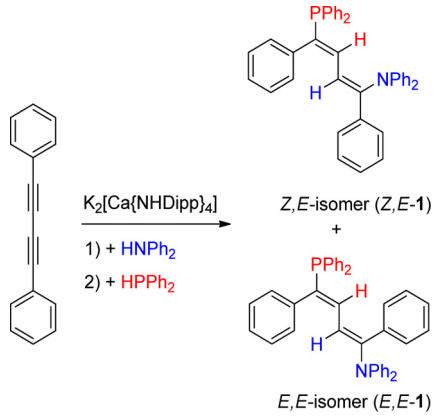
Synthesis and Catalysis. The singly hydroaminated *E* and *Z* isomers of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne[9] were hydrophosphanylated with diphenylphosphane in THF in the presence of 5 mol % $[(THF)_4Ca(PPh_2)_2]$, quantitatively yielding 1-diphenylamino-1,4-diphenyl-4-diphenylphosphanylbuta-1,3-diene (**1**) (Scheme 2). The conversion of the substrates was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The *E*/*Z* isomerism at the amino functionality was maintained, whereas only the *E*-isomeric hydrophosphanylation was observed. After complete reaction, the volume of the reaction mixture was reduced to half of the original volume, and the catalyst was destroyed with methanol. The hydropentelation product **1** was recrystallized from methylene chloride/pentane, giving yellow crystals of *E*/*E*-**1** and *Z*/*E*-**1**.

In another trial, the catalytic hydrophosphanylation of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne was repeated with catalytic amounts of $K_2[Ca\{N(H)Dipp\}_4]$. After complete conversion, the solvent was removed, and the residue was dissolved in methanol to inactivate the calcium catalyst. After removal of the methanol, the residue was dissolved in methylene chloride and filtered to remove the calcium-containing compounds. Thereafter, recrystallization from methylene chloride/pentane again provided yellow crystals of *E*/*E*-**1** and *Z*/*E*-**1** (Scheme 3). This result suggests that the two different hydroelementation reactions can be performed without a change in the catalyst system and without the need to isolate the hydroamination product prior to the hydrophosphanylation reaction.

Scheme 2. Two-Step Synthesis of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1) Using Different Calcium-Based Catalysts for the Hydropentelation Reactions



Scheme 3. Hydroamination and Hydrophosphanylation of Diphenylbutadiyne with the Same Catalyst $K_2[Ca\{N(H)Dipp\}_4]$



Because of the promising finding that $K_2[Ca\{N(H)Dipp\}_4]$ can promote hydroamination and hydrophosphanylation of diphenylbutadiyne, the hydroamination of diphenylbutadiyne was also performed with *N*-methyl-aniline and *N*-methyl-tolylamine as previously published with the catalyst $K_2[Ca\{N(H)Dipp\}_4]$.[9] Diphenylphosphane was added to this reaction mixture, yielding the appropriate hydrofunctionalization products 1-(*N*-methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (**2**) and 1-(*N*-methyl-tolylamino)-1,4-diphenyl-4-diphenylphosphanylbuta-1,3-diene (**3**) according to Scheme 4. Again, the initial hydroamination reaction gave an *E*/*Z*-isomeric mixture, whereas the hydrophosphanylation occurred regio- and stereoselectively to the *E*-isomeric hydrophosphanylation products.

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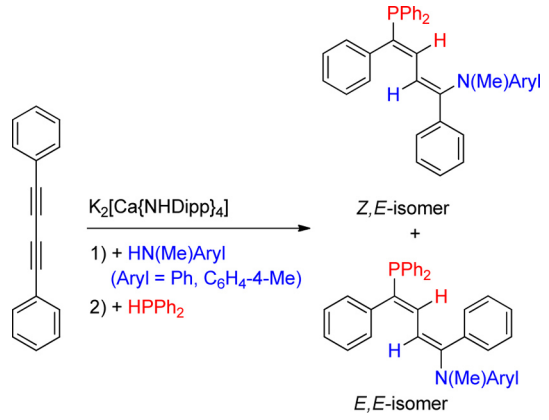
Scheme 4. Calcium-Mediated Synthesis of 1-(*N*-Methylanilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes[a]



[a]Aryl = phenyl (**2**) or *p*-tolyl (**3**).

Isolation of the intermediate hydroamination product 1-amino-1,4-diphenylbut-1-ene-3-yne proved to be advantageous to prevent impurities such as bis-hydroaminated compounds. Unreacted butadiyne also had to be removed prior to the hydrophosphanylation procedures because otherwise the product would also contain bis-hydrophosphanylated derivatives. These side products hamper the isolation of analytically pure 1-amino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene and hence lower the yields. Therefore, the preferred method involves an initial hydroamination reaction catalyzed by $K_2[Ca\{N(H)Dipp\}_4]$, followed by isolation and purification of 1-amino-1,4-diphenylbut-1-ene-3-yne. Thereafter, the hydrophosphanylation of this amine can be performed using catalytic amounts of either $[(THF)_4Ca(PPh_2)_2]$ or $K_2[Ca\{N(H)Dipp\}_4]$. In neither case were *E,Z*- and *Z,Z*-isomeric 1-amino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes observed. This finding is most probably the consequence of steric strain, but electronic effects may also play a minor role.

Molecular Structures. The molecular structures of (*E,E*)-1-diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*E,E*-**1**) and (*Z,E*)-1-(*N*-methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*Z,E*-**2**) are depicted in Figures 1 and 2, respectively, and the structures of *Z,E*-**1** and *Z,E*-**3** are represented in the Supporting Information. Selected structural parameters are compared in Table 1. Regardless of the isomerism, the structural parameters of these compounds are very similar. The butadiene fragment shows no delocalization, and typical C═C and C−C bond lengths of approximately 135 and 145 pm, respectively, are observed. For steric reasons, the planar amino group is twisted toward the planar butadiene plane; therefore, the electron pair at N cannot interact with the π-system of the butadiene moiety. In contrast to the amino group, the phosphorus atom is in a trigonal pyramidal environment with C−P−C bond angles of about 102°. Steric strain between the substituted end groups leads to a distortion of the C−C−C bond angles of the butadiene fragment. The C1−C2−C3 and C2−C3−C4 bond angles of *E,E*-**1** are significantly widened, whereas for all *Z,E* isomers, the enlargement of these bond angles is smaller. This finding verifies an intramolecular steric strain of the *Z,E* isomers smaller than that of the *E,E* derivatives. The lack of interaction between the phosphanyl end groups and the butadiene units leads to very similar P−C bonds of approximately 183 pm to the phenyl

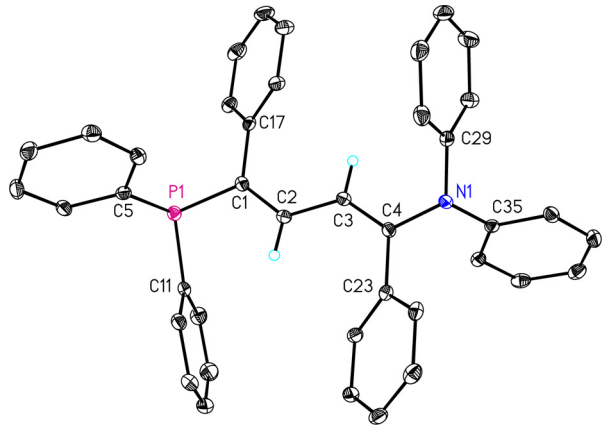


Figure 1. Molecular structure and numbering scheme of (*E,E*)-1-diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*E,E*-**1**). The ellipsoids represent a probability of 30%; H atoms are shown with arbitrary radii.

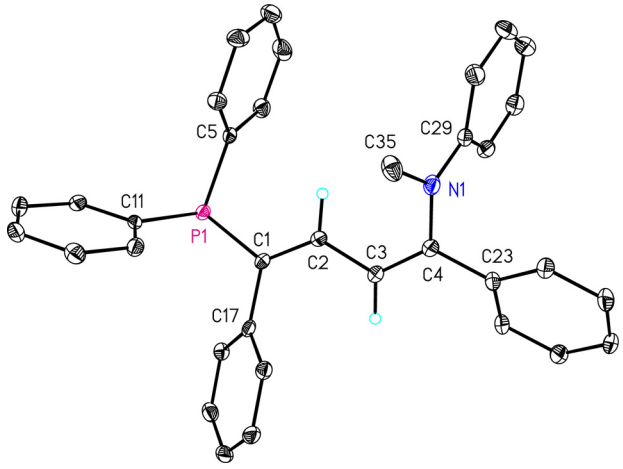


Figure 2. Molecular structure and numbering scheme of (*Z,E*)-1-(*N*-methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*Z,E*-**2**). The ellipsoids represent a probability of 30%; H atoms are drawn with arbitrary radii.

and butadiene moieties in all of these compounds, representing a characteristic P−C single-bond value.

NMR Spectroscopy. Selected NMR parameters of the 1-amino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes are compared in Table 2. The *E/Z* isomerism of the amino group has a small influence on the chemical shifts of the ^{31}P nuclei. Thus, the ^{31}P resonances of the *E,E* isomers are observed at nearly 5 ppm, whereas the *Z,E* isomers show chemical shifts of about 2.5 ppm. The carbon atoms of the butadiene backbone show low-field shifted signals between 135 and 156 ppm. Here, the amino-substituted C4 atoms lie at a field lower than that of the P-bound C1 atoms. The absolute values of the $^nJ_{C-P}$ coupling constants decrease with increasing *n* from approximately 22 Hz (*n* = 1) over 12 Hz (*n* = 2) to 2 Hz (*n* = 3). The vicinal $^3J_{H-H}$ and $^3J_{H-P}$ couplings of the hydrogen atoms at C2 and C3 also depend on the isomerism of the amino group with larger values for the *E,E* isomers.

In agreement with the structural data, the *Z,E*-isomeric forms are the major components, whereas the amount of *E,E* isomers is always significantly smaller. Therefore, we were able to isolate and crystallize the *Z,E* isomers of all reported derivatives,

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Table 1. Selected Structural Parameters of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1), 1-(*N*-Methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (2), and 1-(*N*-Methyl-tolylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (3)

	E,E-**1**	*Z,E*-**1**	*Z,E*-**2**	*Z,E*-**3**
P1−C1	182.9(2)	183.6(2)	183.5(3)	182.7(4)
C1−C2	135.5(3)	134.6(2)	135.2(4)	134.0(6)
C2−C3	144.6(3)	145.0(2)	144.7(4)	144.8(6)
C3−C4	134.9(3)	135.3(2)	135.1(4)	135.6(6)
N1−C4	143.3(3)	142.3(2)	142.0(4)	141.4(5)
P1−C5	182.0(3)	183.6(2)	183.4(3)	182.9(5)
P1−C11	182.3(3)	182.9(2)	183.8(2)	182.9(4)
C1−C17	148.4(3)	148.4(2)	149.3(4)	149.6(6)
C4−C23	148.7(4)	147.6(2)	148.7(4)	148.0(6)
N1−C29	143.5(3)	141.5(2)	139.5(4)	141.2(6)
N1−C35	142.9(3)	142.6(2)	146.1(4)	145.0(6)
C1−P1−C5	102.1(1)	102.10(8)	102.2(1)	103.6(2)
C1−P1−C11	102.7(1)	102.11(8)	103.8(1)	102.7(2)
C5−P1−C11	103.9(1)	102.44(8)	102.5(1)	103.3(2)
P1−C1−C2	122.1(2)	121.7(1)	121.8(2)	123.0(3)
C1−C2−C3	125.2(2)	127.7(2)	126.9(3)	126.5(4)
C2−C3−C4	127.1(2)	122.3(2)	122.1(3)	124.8(4)
C3−C4−N1	118.8(2)	118.8(2)	120.7(2)	120.0(4)
C4−N1−C29	117.3(2)	120.1(1)	120.4(2)	120.8(3)
C4−N1−C35	117.7(2)	119.5(1)	119.5(3)	119.0(4)
C29−N1−C35	118.8(2)	120.1(1)	119.9(3)	118.8(4)

Table 2. Selected NMR Data of the *E,E* and *E,Z* Isomers of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1), 1-(*N*-Methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (2), and 1-(*N*-Methyl-tolylamino)-1,4-diphenyl-4-(diphenylphosphanyl)-buta-1,3-diene (3)

	E,E-**1**	*Z,E*-**1**	*E,E*-**2**	*Z,E*-**2**	*E,E*-**3**	*Z,E*-**3**
			^{1}H NMR			
δ(C2-*H*)	6.39	6.29	6.27	6.01	6.31	6.03
δ(C3-*H*)	6.62	6.45	6.49	6.51	6.49	6.42
^{3}J(H,H)	8.3	5.3	8.2	5.9	8.5	6.0
^{3}J(H,P)	12.1	10.7	11.6	10.9	11.5	10.9
δ(N-CH_3)			3.04	2.82	2.96	2.81
			^{13}C{^{1}H} NMR			
δ(*C*1)	140.6	140.4	141.8	141.1	140.3	142.4
^{1}J(C,P)	23.1	23.1	19.8	22.1	22.2	22.7
δ(*C*2)	136.4	135.0	136.2	136.2	136.1	135.5
^{2}J(C,P)	11.7	12.1	12.3	12.3	10.8	12.4
δ(*C*3)	146.7	145.7	147.5	147.5	146.6	147.0
^{3}J(C,P)	2.5	2.1	2.1	2.1	2.8	2.2
δ(*C*4)	147.5	147.1	151.6	149.5	152.0	156.0
δ(N-CH_3)			40.9	38.1	38	37.5
			^{31}P{^{1}H} NMR			
δ(*P*1)	4.45	2.54	4.70	2.28	4.96	2.35

whereas the parameters of the *E,E*-isomeric compounds had to be elucidated from isomeric mixtures.

Proposed Mechanism. On the basis of these findings, the catalytic cycle had to be formulated as a two-step reaction sequence, and the proposed mechanism is presented in Scheme 5. The initial catalytic cycle is depicted in the bottom part. After addition of the Ca−N bond, the intermediately formed alkenylcalcium complex **A** either deprotonates an amine (formation of the *E*-isomeric alkenylamine) or rearranges via intermediates **B** and **C** to the finally formed *Z*-alkenylamine. The necessity of obtaining the monohydroaminated products **D** and **E** limits the substitution pattern of the secondary amine substrates. For more reactive amines, the second calcium-mediated hydroamination of the other C≡C bond overlaps with the first hydroamination step, yielding mixtures of starting butadiyne and singly and doubly hydroaminated butadienes. In our hands, the above-utilized aniline derivatives represent the preferred substrates.[9] After complete conversion and preferably isolation of the alkenylamines, diphenylphosphane is added, immediately yielding the catalytically active calcium phosphanide species (L represents Lewis bases such as anionic amides and phosphanides or neutral amines, phosphanes, or ethers). The addition of the newly formed Ca−P bond to the remaining C≡C bond yields the intermediates **F** and **G** that immediately deprotonate the still-present diphenylphosphane. This hydrophosphanylation always leads to the formation of *E*-isomeric alkenylphosphanes, as shown in Scheme 5. In contrast to the calcium-mediated hydroamination, the catalytic hydrophosphanylation represents a very fast addition of a phosphane to an alkyne moiety. Under these reaction conditions, neither the amines nor the phosphanes react with the C=C bonds. The sequence of the catalytic steps (first hydroamination, then hydrophosphanylation) must be maintained because the phosphanes always add quantitatively to both C≡C bonds, invariably yielding doubly hydrophosphanylated derivatives.[10]

CONCLUSION

In summary, 1-amino- and 4-phosphanyl-substituted buta-1,3-dienes can be prepared and isolated in moderate to good yields from a calcium-mediated stepwise addition of secondary amines and phosphanes to butadiyne. Both of these hydrofunctionalization reactions can be promoted with the coligand-free calciate K_2[Ca{N(H)Dipp}$_4$] that is easily accessible and stable in the crystalline state as well as in ethereal solvents, allowing the preparation of stock solutions. After inactivation of the catalyst with methanol, pure 1-amino-4-phosphanylbuta-1,3-dienes are obtained by common workup procedures. Even though the same catalyst is used for both hydroelementation steps, the isolation of the intermediate 1-amino-1,4-diphenyl-but-1-ene-3-yne is recommended to ease isolation of the pure end products.

Dipotassium tetrakis(2,6-diisopropylanilino)calciate is an easy-to-handle and effective catalyst for the hydrofunctionalization of C≡C bonds in diphenylbutadiyne with both secondary amines and phosphanes, allowing the synthesis of 1-amino-1,4-diphenyl-4-phosphanylbuta-1,3-dienes. This calciate crystallizes as a coordination polymer; nevertheless, it is soluble in ethereal solvents, enabling the preparation of stock solutions. The crystalline compound and the stock solutions of this complex are stable and can be stored under anaerobic conditions. Both hydroelementation steps are regioselective, but only the catalytic addition of the H−P bond also stereoselectively yields the *E* isomer.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under nitrogen using standard Schlenk techniques. The solvents were dried according to standard procedures prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. The yields given are not optimized. ^{1}H, ^{13}C{^{1}H}, and

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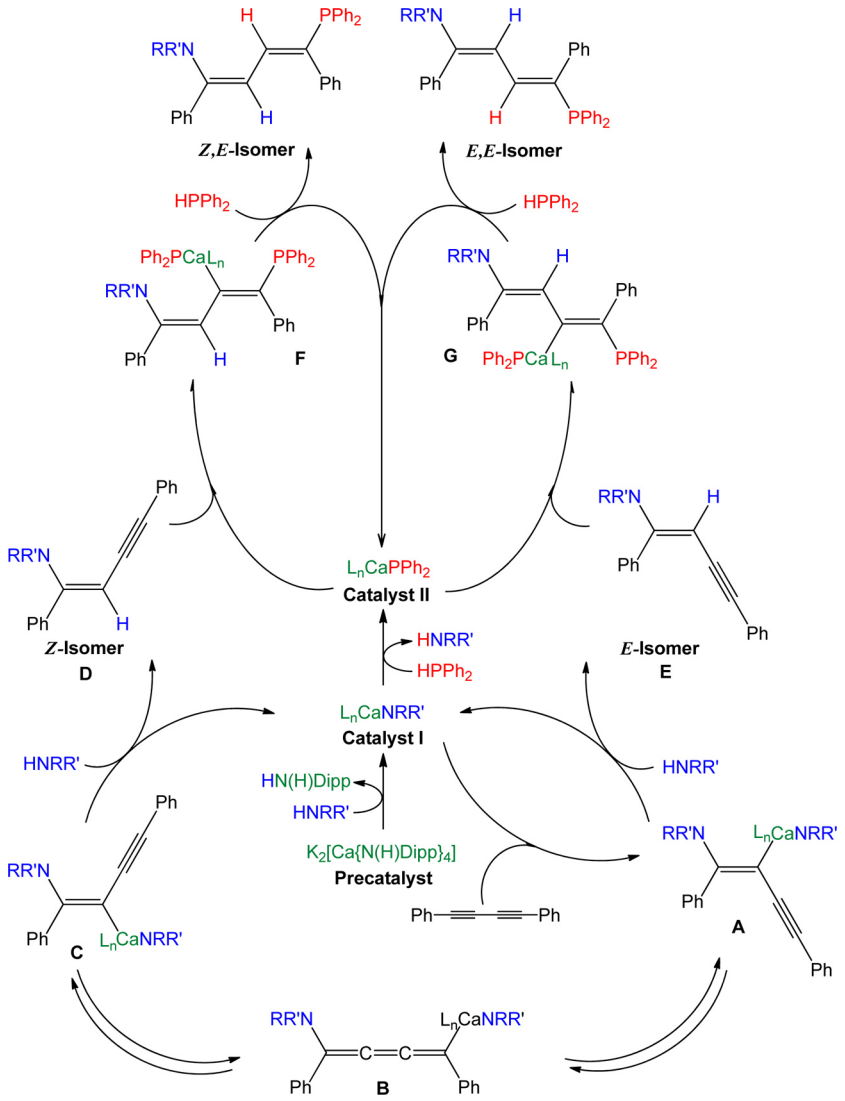
Scheme 5. Proposed Catalytic Cycle Shown as a Two-Step Process of Subsequent Hydroamination and Hydrophosphanylation Reactions[a]



[a]The bottom part shows the hydroamination and offers an explanation for the *Z*/*E* isomerism. In the second hydrophosphanylation catalysis, the amido ligand is substituted by the phosphanido group. The thus-formed Ca−P bond adds to the remaining alkyne moiety, followed by a metalation reaction. L represents a Lewis base such as amido or phosphanido anions or neutral Lewis bases such as ethers, amines, and phosphanes (see text).

$^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker Avance 200, Avance 400, and Avance 600 spectrometers. Chemical shifts are reported in parts per million. In some cases, $^{1}H,^{13}C\{^{1}H\}$-HSQC, $^{1}H,^{13}C\{^{1}H\}$-HMBC, and H,H-COSY NMR experiments were performed for the assignment of the resonances. For mass spectrometric investigations, the spectrometers ThermoFinnigan MAT95XL and Finnigan SSQ710 were used. IR spectra were recorded with a Bruker ALPHA FT-IR spectrometer. The starting amines and calcium-based catalysts $[(THF)_4Ca(PPh_2)_2]$ and $K_2[Ca\{N(H)Dipp\}_4]$ were prepared according to the literature protocols.

Synthesis of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1). In method A, 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne (0.2 g, 0.54 mmol) was dissolved in 8 mL of THF. Diphenylphosphane (0.094 mL, 0.54 mmol) and 5 mol % $[(THF)_4Ca(PPh_2)_2]$ were added. The reaction mixture turned yellow immediately. After being stirred at rt for 2 h and under reflux for an additional 6 h, the volume was reduced to half of the original volume. A few milliliters of methanol were added, and the reaction mixture was stored at −15 °C. Yellow crystals of **3** (0.11 g, 0.2 mmol, 37%, mixture of isomers) precipitated and were collected. After a reduction of the volume of the mother liquor, another crop of crystals was obtained and isolated. In method B, to a solution of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne (0.140 g, 0.376 mmol) in THF (18 mL) were added diphenylphosphane (0.07g, 0.376 mmol) and 5 mol % calciate $K_2[Ca\{N(H)Dipp\}_4]$. The reaction mixture was stirred for 6 h at rt. Afterward, the solvent was removed in vacuo, and 10 mL of anhydrous methanol was added to inactivate the catalyst. Then, the methanol was removed, and 12 mL of dichloromethane was added. This solution was filtered over diatomaceous earth. Crystallization via the diffusion method (dichloromethane/pentane) at 5 °C yielded yellow crystals suitable for X-ray diffraction studies (0.14 g, 0.251 mmol, 67%, mixture of isomers). Mp: 138−142 °C. ^{1}H NMR (600 MHz, THF): δ 7.36 (d, J_{H-H} = 7.2 Hz, 2H), 7.31 (J_{H-H} = 7.7 Hz, 2H), 7.21−7.07 (m, 16H), 7.06−7.01 (m, 4H), 6.88 (m, 6H), 6.66 (d, $^{3}J_{H-H}$ = 7.5 Hz, 1H, *E*,*E*), 6.45 (d, $^{3}J_{H-H}$ = 10.7 Hz, 1H, *Z*,*E*), 6.39 (dd, $^{3}J_{H-P}$ = 12.1, 8.3 Hz, 1H, C2-*H E*,*E*), 6.29 (dd, $^{3}J_{H-P}$ = 10.7, 5.3 Hz, 1H, C2-*H Z*,*E*). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ 147.5 (*C*4 *E*,*E*), 147.3 (*C*4 *Z*,*E*), 146.7 (d, $^{3}J_{C-P}$ = 2.5 Hz, *C*3 *E*,*E*), 145.9 (d, $^{3}J_{C-P}$ = 2.4 Hz, *C*3 *Z*,*E*), 144 (d, J_{C-P} = 16.5 Hz, *C*11,5), 143.4 (d, $^{2}J_{C-P}$ = 6.4 Hz), 140.6 (d, J_{C-P} = 23.1 Hz, *C*1 *E*,*E*), 139.8 (d, J_{C-P} = 23.1 Hz, *C*1 *Z*,*E*), 139.5, 139 (d, $^{2}J_{C-P}$ = 3.5 Hz), 136.4 (d, $^{2}J_{C-P}$ = 11.7 Hz, *C*2 *E*,*E*), 135 (d, $^{2}J_{C-P}$ = 11.6 Hz, *C*2 *Z*,*E*), 134.8, 134.6,

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134.18 (d, $^2J_{C-P}$ = 7.5 Hz), 133.5, 133.3, 129.8, 129.7, 129.4, 129.3, 129.2 (d, ^3J = 2.8 Hz), 129.1, 128.6 (d, $^2J_{C-P}$ = 7.3 Hz), 128.4, 127.8, 127.7, 127.7, 127.6, 126.8, 125.5, 125.1, 122.6 (d, $^3J_{C-P}$ = 2.0 Hz), 122.3, 122.2, 122.1, 122, 121.9, 121.78. ^{13}C NMR (151 MHz, [D$_8$]THF, *Z,E* isomer): δ 147.1 (*C*4), 145.7 (d, $^3J_{C-P}$ = 2.1 Hz, *C*3), 143.9 (d, J_{C-P} = 17.6 Hz, *C*11,5), 140.4 (d, J_{C-P} = 23.1 Hz, *C*1), 138.5, 135 (d, $^2J_{C-P}$ = 12.1 Hz, *C*2), 134.3, 134.2, 133.8 (d, $^2J_{C-P}$ = 7.9 Hz), 129.3 (d, $^2J_{C-P}$ = 9.3 Hz), 128.8, 128.5, 128.1, 128.1, 128, 127.8, 127.1, 127, 122 (d, $^2J_{C-P}$ = 1.7 Hz), 121.8, 121.5. ^{31}P{^{1}H} NMR (243 MHz, [D$_8$]THF): δ 2.54 (s, *Z,E* isomer), 4.49 (s, *E,E* isomer). Elemental analysis ($C_{40}H_{32}NP$, 557.21): Calcd C, 86.15; H, 5.78; N, 2.51; P, 5.55. Found: C, 83.79; H, 5.74; N, 2.51. MS (EI, *m*/*z*): 557 (60) [M], 389 (100) [M − $C_{12}H_{11}N$], 370 (10), 180 (100), 77 (25) [Ph]. IR: 3049 w, 3959 w, 2920 w, 1656 m, 1630 m, 1484 s, 1432 m, 1288 m, 1258 m, 1223 s, 1174 m, 1074 s, 1024 s, 859 m, 797 s, 761 s, 740 s, 690 vs, 602 m, 548 m, 496 s, 479 m.

Synthesis of 1-(*N*-Methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (2). To a solution of 1-(*N*-methyl-anilino)-1,4-diphenylbut-1-ene-3-yne (0.100 g, 0.323 mmol) in THF (17 mL) were added diphenylphosphane (0.06 g, 0.323 mmol) and 5 mol % calciate K_2[Ca{N(H)Dipp}$_4$]. The reaction mixture was stirred for 4 h at rt. After the consumption of all starting materials, all volatile materials were removed in vacuo, and 10 mL of anhydrous methanol was added to destroy the remaining catalyst. Afterward, the methanol was removed, and 12 mL of dichloromethane was added. Then, the solution was filtered over diatomaceous earth. Crystallization via the diffusion method (dichloromethane/pentane) at 5 °C gave single crystals in a yellow mother liquor (0.11 g, 0.222 mmol, 69%). Mp: 146−149 °C. ^{1}H NMR (600 MHz, [D$_8$]THF): δ 7.40 (m, 2H, Ar-*H*), 7.34 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.31−7.13 (m, 24H, Ar-*H*), 6.70 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar-*H*), 6.62 (m, 2H, Ar-*H*), 6.51 (d, $^3J_{H-H}$ = 10.9 Hz, 1H,C3-*H*, *Z,E*), 6.27 (dd, $^3J_{H-P}$ = 11.6, 8.2 Hz, C2-*H*, *E,E*), 6.05−5.97 (dd, $^3J_{H-P}$ = 10.9, 5.9 Hz, 1H, C2-*H*, *Z,E*), 3.04 (s, 1H, C35-*H*, *Z,E*), 2.82 (s, 3H, C35-*H*, *Z,E*). ^{13}C{^{1}H} NMR (151 MHz, [D$_8$]THF): δ 151.6 (C4 *E,E*), 149.5 (*C*4 *Z,E*), 147.5 (d, $^3J_{C-P}$ = 2.1 Hz, *C*3 *Z,E*, *E,E*), 143.9 (d, $^3J_{C-P}$ = 7.6 Hz), 141.8 (d, $^1J_{C-P}$ = 19.8 Hz, *C*1 *E,E*), 141.1 (d, $^1J_{C-P}$ = 22.1 Hz, *C*1 *Z,E*), 139, 136.2 (d, $^2J_{C-P}$ = 12.3 Hz, *C*3 *Z,E*, *E,E*), 135.08 (d, $^2J_{C-P}$ = 20.6 Hz, *C*5,11), 134, 134.7, 134.6, 130.7, 130.3 (d, $^2J_{C-P}$ = 7.8 Hz, C17), 130.1 (d, $^2J_{C-P}$ = 8.7 Hz), 129.5, 129.4, 129.2, 129.1, 129.1, 129 (d, $^2J_{C-P}$ = 4.0 Hz), 129, 128.8, 128.8, 128.7, 128.5, 128.5, 128.3, 127.9, 127.3, 127, 123.1, 122.3, 121.5, 117.9, 114.2, 111.4, 40.9 (C35 *E,E* isomer), 38.1 (C35 *Z,E* isomer). ^{31}P{^{1}H} NMR (243 MHz, [D$_8$]THF): δ 4.70 (s, *E,E* isomer), 2.28 (s, *Z,E* isomer). Elemental analysis ($C_{35}H_{30}NP$, 495.57): Calcd C, 84.82; H, 6.10; N, 2.83; P, 6.25. Found: C, 84.54; H, 6.10; N, 2.86. MS (EI, *m*/*z*): 434 (90) [M], 389 (100) [M − C_7H_9N], 370 (50), 309 (30) [M − L], 183 (90), 118 (70) [$PhNC_2H_3$], 77 (25) [Ph]. IR: 3052 w, 2961 w, 2815 w, 2800 w, 1950 w, 1595 m, 1541 m, 1484 s, 1432 m, 1350 m, 1321 m, 1260 m, 1199 m, 1106 s, 1009 m, 885 m, 775 s, 746 vs, 688 vs, 598 m, 505 m, 498 m, 478 s.

Synthesis of 1-(*N*-Methyl-tolylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (3). To a solution of (*N*-methyl)-(*N*-4-tolyl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine (0.270 g, 0.834 mmol) in THF (17 mL) were added diphenylphosphane (0.156 g, 0.834 mmol) and 5 mol % calciate catalyst K_2[Ca{N(H)Dipp}$_4$], and the reaction mixture was stirred for 8 h at rt. After the reaction solvent was removed, 10 mL of dry methanol was added to deactivate the catalyst. Afterward, the methanol was removed; 12 mL of dichloromethane was added, and the solution was filtered over Celite. Recrystallization via the diffusion method (dichloromethane/pentane) at 5 °C yielded crystals in a yellow solution (0.3 g, 0.588 mmol, 71%). Mp: 147−152 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ 7.43−7.34 (m, 2H), 7.30−7.10 (m, 18H), 6.99 (d, J_{H-H} = 8.2 Hz, 2H), 6.60−6.50 (m, 2H), 6.49 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, C3-*H E,E*), 6.42 (d, $^3J_{H-H}$ = 10.9 Hz, 1H, C3-*H Z,E*), 6.31 (dd, $^3J_{H-P}$ = 11.5, 8.5 Hz, 1H, C2-*H E,E*), 6.03 (dd, $^3J_{H-P}$ = 10.9, 6.0 Hz, 1H, C2-*H Z,E*), 2.96 (s, 3H, C35-*H E,E*), 2.81 (s, 3H, C35-*H Z,E*), 2.27 (s, 3H, C36-*H E,E*), 2.25 (s, 3H, C36-*H Z,E*). ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, *Z,E* isomer): δ 156.2 (*C*4), 147 (d, $^3J_{C-P}$ = 2.2 Hz, *C*3), 142.4 (d, J_{C-P} = 22.3 Hz, *C*1), 138.4, 135.5 (d, $^2J_{C-P}$ = 12.4 Hz, *C*2), 134.5, 134, 129.3, 129.2, 128.5, 128.3, 128.2, 128.1, 127, 127.8, 126.9, 126.5, 125.8, 120, 113.7, 37.5 (*C*35), 19.6 (*C*36). ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, isomeric mixture): δ 156 (*C*4 *Z,E*), 152.8 (*C*4 *E,E*), 147.8 (d, $^3J_{C-P}$ = 2.2 Hz, *C*3 *Z,E*), 146.6 (d, $^3J_{C-P}$ = 2.8 Hz, *C*3 *E,E*), 142.4 (d, J_{C-P} = 22.7 Hz, *C*1 *Z,E*), 140.3 (d, J_{C-P} = 22.0 Hz, *C*1 *E,E*), 139.1 (d, $^2J_{C-P}$ = 12.4 Hz, *C*2 *Z,E*), 138.2, 136.9 (d, $^3J_{C-P}$ = 2.3 Hz), 136.1 ($^2J_{C-P}$ = 10.8 Hz, *C*2 *E,E*), 135.5 (d, $^2J_{C-P}$ = 12.4 Hz, *C*2 *Z,E*) 135.4, 135.2, 135.1, 134.3, 134.2, 134.1, 133.3, 132.3, 131.9 (d, $^2J_{C-P}$ = 9.1 Hz), 131.4, 131.5 (d, $^2J_{C-P}$ = 5.1 Hz), 130.8 (d, $^3J_{C-P}$ = 2.7 Hz), 130.5, 130.3 (d, $^2J_{C-P}$ = 4.8 Hz), 130.1, 129.4, 129.2, 129.1, 129, 128.8, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1 (d, $^3J_{C-P}$ = 2.7 Hz), 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 127, 126.5, 125.8, 125, 120 (d, $^3J_{C-P}$ = 2.3 Hz), 119.7, 117.7, 117.6, 114.5, 113.6, 38 (*C*35 *Z,E*), 37.4 (*C*35 *E,E*), 19.7 (*C*36 *Z,E*), 19.6 (*C*36 *E,E*). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ 4.96 (s, *E,E* isomer), 2.35 (s, *P Z,E* isomer). Elemental analysis ($C_{36}H_{32}NP$, 509.60): Calcd C, 84.84; H, 6.33; N, 2.75; P, 6.08. Found: C, 84.31; H, 6.18; N, 2.75. MS (EI, *m*/*z*): 525 (10) [M + O], 509 (50) [M], 389 (60) [M − $C_8H_{11}N$], 370 (100), 322 (30) [M − L], 183 (100), 118 (60) [$PhNC_2H_3$], 77 (25) [Ph]. IR: 3051 w, 3025 w, 2914 w, 1587 m, 1570 m, 1510 s, 1477 m, 1361 m, 1317 m, 1281 m, 1186 m, 1104 s, 1027 m, 911 m, 806 s, 767 s, 742 vs, 692 vs, 596 m, 557 m, 499 s, 461 m.

Crystal Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K_α radiation. The data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple scans.[12−14] The structures were solved by Direct Methods (SHELXS[15]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[15] All hydrogen atoms (with the exception of the methyl groups of C35 and C36 of compound *Z,E*-**3**) were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.[15] Crystallographic data as well as structure solution and refinement details are summarized in the Supporting Information. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00586. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1457771 for *E,E*-**1**, CCDC-1457772 for *Z,E*-**1**, CCDC-1457773 for *Z,E*-**2**, and CCDC-1457774 for *Z,E*-**3**.

NMR spectra and details for the quantum chemical studies (PDF)

Crystallographic data of the crystal structure determinations (CIF)

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Notes

The authors declare no competing financial interest.

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9 Curriculum Vitae

Personal data

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Place of birth:	Damascus
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Marital status:	Single
Father:	Mouafak Younis, born at 10.01.1957 in Damascus, Syria
Mother:	Fatima Almawardy, born at 25.06.1962 in Damascus, Syria
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Educational history

- January/2012 — Friedrich-Schiller-Universität Jena, Germany
  Ph.D., student, chemistry with Prof. Dr. M. Westerhausen
- September/2007-2011 — Tishreen University, Syria
  Post graduated, Applied Chemistry, and Rating: (good)
  Date of graduation: September **2011**
- July 2007 — Alsaadeh Secondary School, General Secondary Education Certificate, Syria, percentage average 80%

Practical experience

- Properties of (d) elements and their compounds and complexes 2008.
- Automatic analysis, part (1, 2) at Tishreen University, Syria 2009.
- Three months research with laboratory techniques in Friedrich-Schiller-University, Jena, Germany, summer 2010, organized by IAESTE.
- Employee at the scientific office in Sultan Company for Hygiene & Disinfection, Translating scientific articles about various disinfectants from English into Arabic. Doing scientific studies on sterilizing substances, like comparing the effectiveness and characteristics of wounds sterilizing materials, supervising the application of sterilizing materials in many hospitals in Damascus 2011.
- Course about laboratory management (October, 2011) at Damascus university.
- Since 2012 supervising master and bachelor students in different topics such as (organometallic catalytic synthesis as well as organic and inorganic compounds) at Friedrich-Schiller-University, Jena, Germany.
- 2015 two months short term research in Universidade Federal De Viçosa, Brazil.

Awards

- Excellence graduated (certified as Academic excellence). **2009**
- Scholarship for exchange students (DAAD), I.A.E.S.T.E. -Germany, July/**2010**.
- DAAD grant for Ph.D. research April/**2013**
- I.A.E.S.T.E. Germany certificate as member **2014/2015/2016**
- Short-term scholarship (DAAD), I.A.E.S.T.E. -Brazil, October/**2015**.

Languages

Arabic: native language.

Other languages

Language	Understanding	Speaking	writing
English	Very good	Very good	Very good
German	Very good	Very good	Very good
Portuguese	Basic	Basic	Basic

Research interests

Metal-organic chemistry, metal-mediated catalysis.

References

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Publications

1. Jens Langer, Tareq M. A. Al-Shboul, **Fadi M. Younis**, Helmar Görls, Matthias Westerhausen, Coordination Behavior and Coligand-Dependent *cis*/*trans* Isomerism of Calcium Bis(diphenylphosphanides). *Eur. J. Inorg. Chem*. (**2011**), 3002-3007.
2. **Fadi M. Younis**, Helmar Görls, Sven Krieck, Matthias Westerhausen. Synthesis and structural characterization of bis(tetrahydropyran)calciumbis[bis(tri-methylsilyl)amide]. *Z. Anorg. Allg. Chem.* **2013**, 19-21
3. Carsten Glock[§], **Fadi M. Younis[§],** Steffen Ziemann, Helmar Görls, Wolfgang Imhof, Sven Krieck, Matthias Westerhausen. 2,6-Diisopropylphenylamides of Potassium and Calcium A Primary Amido Ligand in s-Block Metal Chemistry with an Astonishing Reactivity. *Organometallics* **2013**, 32, 2649-2660
4. **Fadi. M. Younis**, S. Krieck, H. Görls, M. Westerhausen. S-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines Using a Dipotassium Tetrakis(amino)calciate Precatalyst. *Organometallics* **2015***, 34,* 3577-3585.
5. **Fadi. M. Younis**, S. Krieck, H. Görls, M. Westerhausen. Hydroamination of diphenylbutadiyne with secondary *N*-methyl-anilines using the dipotassium tetrakis(2,6-diisopropylanilino)calciate precatalyst. Dalton Trans., 2016, 45, 6241-6250.
6. **Fadi. M. Younis**, S. Krieck, T.M. A. Al-shboul, H. Görls, M. Westerhausen. Calcium-Mediated Catalytic Synthesis of 1-(Diorganylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes. *Inorg. Chem*. **2016**, 55, 4676-4682.

Conferences

- Congress: The Sixth Jordanian International Conference of Chemistry.
  Date: 19-22 April **2011**.
  Place: Irbid, Jordan.
- Congress: M.A.N.S-10 (Mitteldeutsches Anorganisches Nachwuchs Symposium)
  Date: 20 September **2012**.
  Place: Jena, Germany.
- Congress: M.A.N.S-11 (Mitteldeutsches Anorganisches Nachwuchs Symposium)
  Date: 19 September **2013** (**Lecturer**).
  Place: Dresden, Germany.
- I.A.E.S.T.E. national conference **2012, 2013, 2014, 2015**, Bonn, Germany.
- I.A.E.S.T.E. local committees meeting **2012, 2013, 2014**, **2016** (Cologne, Hamburg, Chemnitz, Freiberg), Germany.
- Congress: M.A.N.S-13 (Mitteldeutsches Anorganisches Nachwuchs Symposium)
  Date: September **2015**.
  Place: Chemnitz, Germany.

Personal Merits

Self-motivated, Positive attitude, Willingness to Learn, Open Minded, Social, work under pressure, patient, Responsible and committed to excellence and success, Multicultural awareness and ambitious.

Habits

Reading, cycling, hiking, swimming, traveling, learning about cultures and languages.

10 Selbstständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

Jena, den ……..

Fadi Younis